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ESTIMATION OF CYANOGEN COMPOUNDS IN CONCENTRATED AMMONIA LIQUOR.*

By PERCY E. SPIELMANN, Ph.D., B.Sc., F.I.C., and HENRY WOOD.

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Determinations of considerable accuracy can be made very simply by a colorimetric method (compare Young, Alkali Inspector's 43rd Rep., 1906, p. 42), by employing the Lovibond tintometer.

The substances to be estimated are:—Ammonium thiocyanate: highest percentage met with 0·185 per cent, average quantity about 0·06 per cent. Ammonium cyanide ("volatile cyanide"): highest percentage met with 0·024 per cent. Ammonium ferrocyanide: highest percentage met with 0·44 per cent, average quantity about 0·1 per cent.

The usual titration method for estimating thiocyanate as cuprous thiocyanate is scarcely admissible in the present connection, mainly on account of the end point being somewhat troublesome (*loc. cit.*, p. 47); thus the percentage of ammonium thiocyanate found in two successive examinations in concentrated ammonia liquor was 0·0538 per cent and 0·0526 per cent, and in crude liquor 0·237 per cent and 0·275 per cent.

Feld's method for estimating cyanide can be employed, but it is somewhat tedious; and it is necessary to modify it—on account of the large quantity of ammonia present—after adding to the liquid 50 cc. of concentrated lead nitrate solution, by neutralising the remaining ammonia by running in 2/N nitric acid, until a little lead hydroxide still remains undissolved. Distillation and titration are then proceeded with as usual.

Feld's method of estimating ferrocyanides, though applicable, is lengthy and cumbersome as compared with Williams' elegant reaction with cuprous chloride (*Journ.*, 1912, 468).

The basis of this scheme of analysis which is being advocated is the following:—

1. Conversion of the ammonium thiocyanate into ferric thiocyanate and measurement of the depth of colour obtained.

2. Interaction of a further quantity of the original liquid with ammonium polysulphide, whereby the ammonium cyanide originally present is converted into ammonium thiocyanate, and the estimation of the total ammonium thiocyanate as ferric thiocyanate. The increased quantity found over and above that found directly (without polysulphide treatment) is a measure of the quantity of cyanide originally present.

The presence of ferrocyanide compounds causes no complication, as the conversion of any proportion of the ferrocyanide into thiocyanate by the polysulphide solution can be avoided.

After a considerable number of experiments and trials on known mixtures and on commercial samples, the following procedure is recommended, and it is advised that details be closely adhered to.

Estimation of Ammonium Thiocyanate.—10 cc. of the sample is run into about 40 cc. of water and the liquid is acidified with dilute sulphuric acid, shaking and cooling being continuous all the time. Iron alum is added until the liquid becomes red in colour, and it is then warmed to coagulate the precipitate. It is allowed to stand for half an hour, and after filtering and washing the precipitate, and cooling, 10 cc. of acid solution of iron alum (100 cc. of saturated alum solution with 10 cc. of concentrated nitric acid) is added, the volume is made up to 100 cc., and the liquid examined in the tintometer.

If the depth of colour is too great, the liquid must be diluted by taking 50 cc., adding 10 cc. more of the acid alum solution, and making up to 100 cc. If this further addition of iron alum be not made, the dilute solution is less than half as deep in colour as the stronger solution.

Estimation of Ammonium Thiocyanate together with Ammonium Cyanide, after Conversion of the latter into Thiocyanate.—If ferrocyanide is absent, 10 cc. of the sample is run into a little water, ammonium polysulphide solution is added until the liquid is distinct yellow, and the mixture is diluted to 100 cc. The polysulphide solution is made (Alkali Inspector's Rep., 1906, p. 47) by diluting 200 cc. of 0·880 ammonia to one litre, saturating half of this with hydrogen sulphide, adding the other half of the diluted ammonia solution, and then saturating with sulphur (which takes about a week). The liquid under examination is then heated to boiling-point, whereby all ammonia is driven off, treated with iron alum as before, and examined in the tintometer. The difference between this reading and that obtained for thiocyanate alone gives, by simple calculation, the percentage of cyanide in the original sample.

During the boiling stage, the precipitated sulphur occasionally becomes greenish. This does not indicate that there is necessarily any appreciable quantity of ferrocyanide in the precipitate; it may be due to a very small trace of sulphide of iron.

Estimation of Ammonia Cyanide when Ferrocyanide is present.—The removal of the ferrocyanide is carried out as follows: 25 cc. of the sample is run into polysulphide solution which is to be kept in excess as judged by its yellow colour. After standing for twenty minutes the liquid is acidified with dilute sulphuric acid, with continuous shaking and cooling (the latter precaution is important), and iron alum is added until the liquid becomes reddish in colour. It is then warmed (not above 60° C.) to coagulate the ferrocyanide precipitate; this is helped by the addition of a few crystals of sodium sulphate. After standing for half an hour, the precipitate is filtered off and washed as usual, and 50 cc. of acid iron alum is added to the filtrate. If the volume of the latter is about 500 cc. or more, a small addition of nitric acid is advisable.

The different procedures recommended for the estimation of thiocyanate and cyanide, when ferrocyanide is or is not absent, result from the necessity of avoidance of heating when ferrocyanide and polysulphide (added or original) are present together, or when cyanide may react, undesired, with polysulphide. It would be perfectly feasible, however, to employ the method given for the determination of cyanide when ferrocyanide is present to a sample when the latter is absent, but the procedure recommended is a quicker one.

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The applicability of the method, and its limitations, are shown by the following figures obtained from known mixtures:—In 5 cc. of a solution of potassium ferro-

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cyanide containing 0·01840 grm. and 5 cc. of N/100 solution of ammonium thiocyanate the amount of ferrocyanide found was 0·01842 grm., whilst the same colour was obtained as when 5 cc. of thiocyanate solution was examined alone.

The behaviour of ferrocyanide towards polysulphide solution was tested by preparing a solution of ammonium ferrocyanide by precipitating a known quantity of potassium ferrocyanide with excess of iron alum, treating the washed precipitate with ammonia (sp. gr. 0·880), and converting into thiocyanate by boiling with polysulphide solution. The experiments showed that when ferrocyanide is present in only a very small quantity, the whole of it may be converted by the "hot method" into ammonium thiocyanate, making the cyanide figure too high; when, however, the ferrocyanide is present in a quantity above 0·001 per cent, an indefinite portion is converted, rendering results incapable of interpretation. The whole trouble may be avoided by using the "cold method."

Here the authors are in disagreement with Linder, who advocates (Alkali Inspector's 54th Rep., 1917, p. 25) boiling off the excess of volatile ammonium compounds from the mixture after reaction in the cold; their general experience of the reaction may be exemplified by the following figures obtained with a commercial sample:— Ferrocyanide, 0·0682 per cent; cyanide, absent; thiocyanate, running into boiling water (Linder's method), 0·180 per cent; boiling down, as usual, 0·180 per cent; by "cold method," 0·178 per cent; polysulphide, and boiling down (Linder's latest method), 0·300 per cent.

Without going further into the subject, it is of value to remember that the ferrocyanide precipitate appears to vary greatly in commercial samples of concentrated ammonia liquor, both in the ease or obstinacy of its appearance and formation, and in the velocity of its decomposition by sodium hydroxide.

Two artificial mixtures were made up and examined with the following results:—

No. 1.

	Taken.	Found.
Ammonia 0·880	70 cc.	19·35 p.c.
H_2S passed in	—	1·25 p.c.
Ammonium thiocyanate solution	10 cc. = 0·076 p.c.	0·076 p.c.
Hydrocyanic acid (as KCN)	10 cc. = 0·0151 p.c.	0·0164 p.c.
Ammonium ferrocyanide solution	10 cc. = 0·0284 p.c.	0·0284 p.c.
Water	—	—

No. 2.

	Taken.	Found.
Ammonia 0·880	50 cc.	14·25 p.c.
H_2S passed in	—	0·248 p.c.
Ammonium thiocyanate solution	10 cc. = 0·076 p.c.	0·074 p.c.
Hydrocyanic acid (as KCN)	1 cc. = 0·00151 p.c.	0·00141 p.c.
Ammonium ferrocyanide solution	5 cc. = 0·0076 p.c.	0·0076 p.c.
Water	34 cc.	—

The small discrepancies between the qauntities taken and found are within the limits of accuracy of the method.

Estimation of Polysulphide.—Linder has described (Alkali Inspector's 54th Rep., 1917) how polysulphide in a sample of concentrated ammonia liquor can be estimated by its reaction with excess of cyanide to form an equivalent quantity of thiocyanate. This can obviously be determined by means of the tintometer, when the procedure would be the following:— (1) Determination of thiocyanate as such; (2) Addition of excess of cyanide solution and boiling as described above. In this case reaction of existing cyanide and ferrocyanide is of no consequence, as the final result is the conversion of polysulphide into thiocyanate. The difference between the two results is the measure of polysulphide in terms of thiocyanate.

Mode of Employment of Tintometer.

In the usual practice of colorimetric methods it is customary to compare the colour obtained experimentally with that given by a known strength of the substance which is being estimated, and this usually entails making up at least one fresh standard for each experiment or batch of experiments.

When a tintometer is available and a considerable number of samples have to be examined, it is economical in time and trouble to measure once for all the depth of colours of known mixtures of various strengths and to record them on squared paper, so that any subsequent colour can be compared with the graph so constructed. In the present case the authors had a Lovibond tintometer in use, and this was found to be a very suitable instrument for the purpose.

The instrument was set up pointing to the interior of a box blackened on the inside, with a strip of truly white paper opposite the e d of the instrument. Extraneous light was excluded from the front opening by a curtain of black velvet. Inside, a half-watt lamp was used as a source of illumination, screened with three thicknesses of truly white tissue paper in order to temper the light to a suitable intensity.

Measurements of depth of colour are made by matching the tint of the liquid with red and yellow glasses, but as a considerable latitude was found to be associated with the yellow colour, the strength of thiocyanate is best plotted against the red colour units only.

In making up the standard colours the following quantities of ammonium thiocyanate were taken, treated with acid iron alum and diluted to 100 cc. 1 cc. of N/10 ammonium thiocyanate contains 0·0076 per cent of the salt. Suitable quantities were diluted and measured in three cells, giving three different thicknesses of liquid.

Cells.	Ammonium thiocyanate. Per cent wt./vol.	Red units.
⅛ in.	0·0019	1·3
	0·0076	4·6
	0·0300	13·65
½ in.	0·0019	4·6
	0·0038	7·6
	0·0076	11·9
1 in.	0·0019	7·6
	0·0038	13·0

It was found that above 12 or 13 units the colour was so deep that matching became uncertain. If colours requiring stronger glasses than those given are obtained they must either be measured in the cell of less thickness or further diluted (see *ante*).

It was found that under the conditions of testing the known solutions, the limit of sensitiveness of the eye was 0·15 red unit in the ½" and in the ⅛" cell, which is equivalent to 0·00021 per cent ammonium thiocyanate and 0·00007 per cent hydrocyanic acid. Therefore the figures found are as close as is possible.

The source of light was standardised on a solution of potassium bichromate, saturated at 20° C., in order that the present work and all other work with colours of the same order can be referred to a definite standard.

Source of illumination.	Cell.	Red units.	Yellow units.	Intrinsic brightness above standard (not affecting depth of colour).
½-Watt-lamp (*a*)	⅛ in.	5·8	16·5	0·01
	½ in.	10·8	34·0	0·02
Daylight.. ..	⅛ in.	8·0	38·0	—
	½ in.	13·25	38·0	—

(*a*) Two different lamps were tested and found to be alike.

The following points in connection with the tintometer reading should be noticed:—Increased thickness of tissue paper for tempering the source of light increases the amount of standard yellow for matching the experimental liquid. A lamp with frosted glass is preferable to a plain glass bulb shielded with tissue paper. If the liquid is intrinsically brighter than the colour glasses neutral tint should be added, after which matching of colour is more reliable.

We take pleasure in acknowledging the courteous manner in which the experience of the Tintometer, Limited, has been placed at our disposal.

Discussion.

Dr. H. G. Colman said that his experience with colorimetric methods for thiocyanate had not been sstisfactory, testing with solutions containing known amounts of thiocyanate, but he had not tried the method using the tintometer, which might be more accurate. He asked the author whether with liquids such as these, containing phenols, the pink colour resulting from the action of the ferric salt on these did not interfere with the test, and whether phenols were added in testing the check solutions. He also asked if hydrogen sulphide was present in the check tests given for cyanide, as he and Yeoman had always obtained low results in its presence, although in its absence the results were satisfactory.

Dr. Spielmann, in reply, stated that it had been substantiated by direct experiment that the colour given by even 1 per cent of phenol and the subsequent addition of a little cresol had no appreciable detrimental effect on the method of analysis. In regard to the presence of hydrogen sulphide when making check tests it would be seen from the two examples given in the paper that this was present in both cases.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D Sc.

The field of physical chemistry, although now fully recognised as an integral part of chemical knowledge, has sometimes been regarded as lying entirely apart from that of industrial activity. This is a complete misconception, for while the influence of physical chemistry on the conduct of technical processes in the chemical and allied industries is, no doubt, indirect in the majority of cases, it is none the less real and extensive. Physical chemistry is concerned mainly with general underlying principles, but its development has contributed in a notable degree to the further advancement of chemical knowledge from the purely descriptive to the rational and quantitative stage. This is abundantly evident in the recent history of inorganic chemistry. Important reactions between well-known substances, reactions which twenty or thirty years ago were well understood in a general way, have been explored afresh in the light of physico-chemical principles, and an enormous amount of valuable quantitative data has been accumulated in this renascence of inorganic chemistry.

In the chemical and allied industries, as elsewhere, one main element in progress and development is the gradual substitution of quantitative knowledge for qualitative, and the displacement of rule-of-thumb, haphazard methods by those which are based on scientific principles, and therefore permit intelligent control. In the advance so far made along these lines physical chemistry has played no small part, and it is the object of these lectures to emphasise and illustrate some of the physico-chemical principles which have a definite bearing on industrial processes.

One of the main directions in which physical chemistry has led to a clearer perception of the optimum conditions and the working limits of technical operations is in connection with chemical equilibrium. Up till a comparatively recent time the best known chemical reactions were of the type which may be described as "complete" in the sense that the change proceeds until one at least of the necessary reacting compounds has been used up and has disappeared. This, perhaps, is not surprising, for the object of analytical chemistry—one of the prominent practical branches of the science—is to discover precisely those reactions which are complete, involving the quantitative conversion of some one substance into another. It is on the quantitative character of the change that the possibility of accurate analysis depends.

Physical chemists, however, have directed attention specially to those numerous reactions which may be described as "incomplete," in that the change stops short of the entire disappearance of any one of the reacting substances, and all the parties to the reaction are represented in the mixture finally obtained. A state of balance or equilibrium between the various substances concerned is established, and the reaction is accordingly termed an "equilibrium" or "balanced" reaction. In such cases it is further found that if the reaction products, or the "resultants," as they may be called, are brought together, they also interact to produce the original substances. The reaction, that is, may proceed in either direction, according to the relative proportions of the compounds concerned, and it may therefore be fairly described as a "reversible" reaction. It is customary to indicate the existence of this reversibility in any particular case by the use of a double arrow instead of the sign of equality, thus: $A+B \rightleftharpoons C+D$.

The further question now arises as to the factors which determine the position of the equilibrium in a reversible reaction, and to this question physical chemistry can supply a quantitative answer. Suppose, for instance, that the substances A, B, C, and D in the foregoing reaction are gases. Then, in accordance with the kinetic conception of the gaseous state, one must picture the molecules in a mixture of the four substances as in a constant state of motion, continually colliding with one another and impinging on the walls of the containiug vessel.

Now chemical action between A and B will be possible only when a molecule of A collides with a molecule of B, and the progress of the change denoted by the upper arrow will depend on the number of these collisions occurring per unit of time—*i.e.*, on their frequency. The frequency of collision, on the other hand, will be proportional to the numbers of the molecules of the substances A and B which are present in unit volume—*i.e.*, to their concentrations. Hence, if the change is resolved into two component opposed reactions $A+B \rightarrow C+D$ and $C+D \rightarrow A+B$, and if v_1 denotes the velocity of the former reaction and v_2 that of the second, then $v_1 = k_1 ab$, and $v_2 = k_2 cd$, where a, b, c, d are the concentrations of the four molecular species A, B, C, and D at the moment considered, and k_1, k_2 are proportionality factors. These formulæ are the algebraic expression of the law of mass action.

For an observer it is not possible to isolate and follow the separate component velocities; he can determine only the net velocity of the total change—*i.e.*, $v_1 - v_2$. As the reaction approaches its position of equilibrium, $v_1 - v_2$ becomes smaller and smaller, and, finally, when equilibrium is established, $v_1 - v_2 = 0$. This does not mean that the reaction mixture is in a condition of stagnation, that all collisions and interchanges have ceased; it means only that there is as much change in the one direction as in the other.

At equilibrium, then, $v_1 = v_2$ or $k_1 ab = k_2 cd$, a, b, c, and d being now the concentrations of A, B, C, and D in the equilibrium mixture. This equation may be written

* Canton Lecture (I.). Delivered before the Royal Society of Arts, December 2, 1918. From the *Proceedings of the Royal Society of Arts*, lxvii., No. 3430.

$k_1/k_2 = cd/ab$, or, since the ratio of two constants is itself a constant, $K = \frac{cd}{ab}$. This quantity K is termed the "equilibrium constant" of the reaction, and its numerical value defines the position of equilibrium for $A+B \rightleftharpoons C+D$ at the temperature considered. This argument may be generalised, and the law of mass action leads to the conclusion that, however the individual concentration values may vary, $\frac{Y}{X}$ = const. at any given temperature, where X is the product of the equilibrium concentrations of the substances on the left-hand side of the equation, and Y is the product of the equilibrium concentrations of the substances on the right-hand side.

These considerations may be applied in the first case to the well-known and technically important equilibrium between sulphur dioxide, oxygen, and sulphur dioxide. This may be represented as $2SO_2+O_2 \rightleftharpoons 2SO_3$, and is the reaction utilised in the large scale production of sulphuric acid by the so-called contact process. It has long been known that sulphur dioxide and oxygen, if passed together over heated platinum, combine to a large extent to form sulphur trioxide, and, indeed, an English patent for such a process was taken out in 1831. Many decades passed, however, before the process was satisfactorily established on the manufacturing scale, the delay being mainly due to difficulties experienced in purifying the sulphur dioxide and in keeping the platinum in full activity as an accelerator of the change.

In the last few years this contact process for the manufacture of sulphuric acid, previously exploited mainly in Germany, has undergone a rapid development in this country, and large quantities of "oleum," essential for the production of explosives, have been turned out. Sulphuric acid, however, is in large demand also in the times of peace, and it may be hoped that the various contact plants laid down under the pressure of war conditions will have a *role* to play when things are normal once again.

The possibilities and limitations of the contact process for sulphuric acid production cannot be thoroughly appreciated except on the basis of the principles of chemical equilibrium. These principles make it possible to formulate definitely the extent to which the equilibrium will be affected by varying the quantities of the reacting substances, and by altering the pressure and the temperature.

In the first place the law of mass action may be applied, on the lines already indicated, to the reversible reaction, $2SO_2+O_2 \rightleftharpoons 2SO_3$, or, as it may be written alternatively, $2SO_3 \rightleftharpoons 2SO_2+O_2$. If c_{SO_3}, c_{SO_2}, and c_{O_2} represent the concentrations of sulphur trioxide, sulphur dioxide, and oxygen at the point of equilibrium, then $\frac{c^2_{SO_2} \cdot c_{O_2}}{c^2_{SO_3}} = K$, the value of which should be constant at a given temperature, irrespective of variations in the relative quantities of sulphur dioxide and oxygen initially used.

The validity of the foregoing mass action formula has been strikingly verified by an investigation in which mixtures of sulphur dioxide, oxygen, and nitrogen in varying proportions were passed through heated quartz vessels containing spongy platinum. The rate of flow was regulated so that the gases were long enough in contact with the hot platinum to attain the condition of equilibrium, and the values of c_{SO_3}, c_{SO_2}, c_{O_2}, the equilibrium concentrations, were deduced from a chemical analysis of the issuing gas mixture. Some results obtained at 727° may be quoted in order to show how closely the mass action formula represents the actual composition of the equilibrium mixture. In the following table, which embodies these results, the first three columns state the relative proportions of the gases (sulphur dioxide, oxygen, and, in some cases, nitrogen) present in the initial mixture employed in each experiment: $2SO_3 \rightleftharpoons 2SO_2+O_2$ at 727°.

Initial Gas Ratio.

SO_2.	O_2.	N_2.	$K \times 10^3$.
0·21	1	—	3·49
0·62	1	—	3·59
1·20	1	—	3·48
1·68	1	—	0·51
3·97	1	—	3·67
1·23	1	3·76	3·60
1·31	1	3·76	3·54
1·55	1	3·76	3·52
	Mean ..	.. .. ..	3·55

As shown clearly by these figures the value of K is independent (1) of the relative proportions of sulphur dioxide and oxygen in the initial gas mixture, and (2) of the presence or absence of nitrogen. In the course of the experiments it was further shown that the value of K obtained with a particular gas mixture was independent of the direction in which the equilibrium point was reached, and of the rate at which the gas was passed. It appears therefore that the mean value of K above may fairly be taken as a quantitative expression of the relation which at 727° exists between the equilibrium concentrations of the various substances concerned in the reaction.

When similar investigations are made at a series of different temperatures the values of K are found to exhibit a regular increase with rise of temperature, and thus form a record of the way in which the equilibrium shifts as the temperature conditions alter. The following table embodies the results of such experiments carried out at various points between 528° and 897° C.:—

$2SO_3 \rightleftharpoons 2SO_2+O_2$ *at Different Temperatures.*

Temp. C.	$K \times 10^3$.
528°	0·015
579°	0·077
627°	0·32
680°	1·12
727°	3·55
789°	12·6
832°	28·0
897°	81·6

If it is borne in mind that $K = \frac{c^2_{SO_2} \cdot c_{O_2}}{c^2_{SO_3}}$, the increase of K revealed by the foregoing figures plainly means that with rising temperature the equilibrium is shifted more and more in favour of the system $2SO_2+O_2$; *i.e.*, the dissociation of sulphur trioxide steadily increases.

From the values of K just tabulated it is easy to trace a graph representing the relation between K and the temperature, and from this to read off the value of the equilibrium constant at any desired point, such as 500° or 600°. The numerical value of K at this point being known it is then possible to calculate for any initial mixture of sulphur dioxide, oxygen, and nitrogen, what will be the composition of the equilibrium mixture; that is, to evaluate the mixture quantity—the "yield"—of sulphur trioxide obtainable under the given conditions. A series of such figures (see following table) shows clearly what are the optimum conditions—so far as the influence of temperature on yield is concerned—for the production of sulphuric acid by the contact process:—

Percentage Composition of the Initial Gaseous Mixture.

SO_2.	O_2.	N_2.
10·1	5·05	84·85
7·0	10·0	83·0
4·0	14·6	81·4
2·0	18·0	80·0

Percentage Conversion of Sulphur Dioxide to Trioxide at—

400°.	500°.	600°.	700°.
96·2	83·2	59·1	31·9
99·3	93·4	73·3	42·5
99·4	94·9	78·3	48·1
99·5	95·6	80·5	51·3

The figures just presented furnish the material for testing an interesting deduction that may be drawn from the *equilibrium formula*. If this is written in the form—

$$\frac{c^2_{SO_3}}{c^2_{SO_2}} = \frac{1}{K} \cdot c_{O_2} \text{ or } \frac{c_{SO_3}}{c_{SO_2}} = \frac{1}{\sqrt{K}} \cdot \sqrt{c_{O_2}},$$

it is plain that the proportion of trioxide to dioxide in the equilibrium mixture, at a given temperature, is proportional to the square root of the oxygen concentration, and will therefore rise as the latter is increased. This conclusion is confirmed by the figures in the table, for it is seen that, as the percentage of oxygen in the initial mixture increases relatively to that of the sulphur dioxide, the percentage conversion goes up.

(To be continued).

THE PERMANENT MARKING OF GLASS VESSELS.

By JOSEPH C. BOCK.

IT is very often desirable and frequently necessary for the chemist to mark glass vessels permanently. This is usually done by means of a diamond or hydrofluoric acid. While the latter procedure gives good results if done carefully, it is a rather troublesome and lengthy process. The use of the diamond requires considerable practice in order to produce good markings, besides it is not always advisable to use it. A preparation called Diamond Ink, usually a mixture of ammonium fluoride, hydrofluoric acid, and barium sulphate, produces permanent marks and is easily applied. It is, however, difficult to obtain sharply defined markings with this method; furthermore the writing is not clearly visible if the surface becomes wet.

The present note proposes the use of glass colour fused in the glass by means of an ordinary burner. In glass painting, the glass colours, mostly mixtures of low fusing silicates and metallic oxides, are mixed with some vehicle and applied to the glass. They are then "fired" in a kiln at a temperature not exceeding 590° C. (Seger cone 022). This procedure is, of course, not applicable as such to ordinary laboratory conditions.

As the "firing" in the present method is done by means of a burner, many of the glass colours could not be used, because they undergo chemical changes when exposed to the flame.

In order to apply to the colours they are intimately mixed with a vehicle (made up of four parts copaiba balsam, one part clove oil, one part lavender oil). (The colours used are obtainable from the Roessler and Hasslacher Chem. Co., Ceramic Dept., Perth Amboy, N.J.—N. Y. Office, 100 Williams Street. The oil can undoubtedly also be obtained there. Many stores handling colours for china painting will have these materials on hand). The colours which have been found most suitable are—Green 728 D, Blue 1079 D, and a mixture of Brown 695 D, and White Enamel 1310 D. (Numbers refer to Roessler and Hasslacher products). The Brown alone can only be used on hard glass or porcelain where higher temperatures can be applied.

The actual procedure is herewith described—The glass colour (use Green 728 D) in powdered form is mixed with just enough of the oil, so it will still run from a pen. (Mixing can be done on a glass plate with a small spatula. Where a small amount of work is contemplated the indentations of an indicator tile have been found useful). A so-called crow-quill (steel) pen is recommended, a fine brush is also very good, but more difficult to handle. The desired markings are made on the clean glass surface. The marked article is then warmed evenly over a flame to dry the oil and also to prevent cracking in the final heating. The place were the marking has been made is now heated by holding against the *side* of the flame of a burner, the flame touching the marking on a tangent, the article being rotated part of a circle. (A Méker burner has been found best. The article should best be held near the base of the flame). During this heating the mark is watched carefully. The colour will first turn black through the carbonisation of the oils, then it will begin to glow a dull red. At this point the article is removed, allowed to cool a little and reheated until the markings, not the glass, again begin to glow.

The marking so obtained presents a smooth, shiny surface. It cannot be removed by mechanical or the usual chemical means. We consider the marking successful, when it cannot be removed mechanically (scratching or scouring), after a twenty-four-hour immersion in "cleaning mixture."

The paint should be mixed as thick as practicable. The heating must be done carefully to avoid caving in or other distortions of the vessel. If porcelain crucibles are to be marked the colour is applied as indicated above, the vessel is then heated in the usual way on a triangle over a free flame.

It may be of interest to mention some of the uses to which this procedure has been put. We have graduated test-tubes for special work, *p.e.*, for Benedict's colorimetric sugar method (12·5 cc. and 25 cc.) or graduated test-tubes to replace small graduated cylinders. Pipettes were graduated in the laboratory. Kjeldahl flasks may be marked to indicate the maximum volume to which they may be filled (students use). Beakers were graduated in 50 cc. or 100 cc. intervals. It is also advantageous to graduate distilling flasks roughly, to know the approximate liquid contents in the course of evaporation. The proposed procedure is especially valuable in the last mentioned instances, because any deep etching or engraving weakens the vessel.

The most difficult problem is the marking of microscope slides. Their heating requires great care and considerable experience in order to avoid an undue amount of breakage. They must be heated *over*, not on the side of a burner, the marked side towards the flame. It is our opinion that a muffle should be used where a large amount of slides are to be marked, using a strip of zinc (m. p. 412° C.) and a Seger cone 022, to indicate the temperature limits. Since a muffle furnace was not available we were unable to carry out this experiment. The marked slides, after being thoroughly dried, may be sent to some shop where glass firing is done and finished there for a nominal charge. (A semi-permanent marking medium can be obtained by mixing a pigment—lead oxide, lampblack, &c.—with a good spar varnish, canada balsam or collodion varnish—banana liquid. It will resist the ordinary cleaning and has been found useful for making stock bottles and similar containers).

[NOTE.—This method of marking vessels has been in use for many years at Sir William Crookes's laboratory for marking small porcelain crucibles and the quartz vessels used in fractional crystallisation of radio-active compounds. Enamel paints of various colours can be purchased at any good artist's colour shop, and it only needs

to be applied with a pen or a fine brush; the vessel is then heated to dull redness over a Bunsen or in a small muffle, and the mark becomes indelible].—*Journal of the American Chemical Society*, xli., No. 3.

THE USE OF ORTHO TOLIDINE AS A COLORIMETRIC TEST FOR GOLD.*

By W. B. POLLARD,
Government Analytical Laboratory, Cairo.

Ortho-tolidine dissolved in dilute acetic acid was suggested by E. B. Phelps (Bulletin No. 1, Ohio State Board of Health, January, 1913) as a delicate colour test for free chlorine in water. This test was modified by J. W. Ellms and S. J. Hauser (*Analyst*, 1914, xxxix., 454), who showed that a hydrochloric acid solution of ortho-tolidine was better adapted for the purpose. Their reagent was prepared by dissolving 1 grm. of ortho-tolidine in a litre of 10 per cent hydrochloric acid.

This reagent in its modified form has now been found to be a delicate test for aurichloric acid. A solution of 1 part of gold in a million parts of water gave a bright yellow colour on addition 1 cc. of the reagent. With a solution containing 1 part of gold in 20 million parts of water the yellow colour can just be detected in a depth of 10 cms. of liquid.

Ellms and Hauser found that in the case of dilute solutions containing free chlorine the colour took about three minutes to fully develop, and was then permanent for about half an hour, after which it slowly faded. This was also found to be the case with aurichloric acid.

In making the test large amounts of strong mineral acid should not be present as the reaction becomes less delicate.

The following metals, when present as chlorides in a dilute hydrochloric acid solution, were found to give no reaction with ortho-tolidine:—Al, Sb(ic), Ba, Bi, Cd, Ca, Cr, Co, Cu, Ir, Pb, Mg, Hg, Mn(ous), Ni, Pt, K, Rh, Na, Sr, Sn(ic), U, and Zn.

In a second paper Ellms and Hauser point out that iron in the ferric condition also reacts with ortho-tolidine. The author found that in the case of ruthenium a yellow colour was also formed. Osmic acid gives a yellow colour, but this changes to green on standing. Vanadates acidified with dilute hydrochloric acid give a reaction. Molybdates acidified with hydrochloric acid do not react.

Sodium tungstate acidified with dilute hydrochloric acid gives a precipitate on addition of ortho-tolidine, but no yellow colour develops.

In preparing standard chlorine solutions Ellms and Hauser found that it was necessary to employ specially purified distilled water. This was not found to be so necessary in the case of gold solutions. The more dilute gold solutions should, however, only be prepared when required, and should contain a small amount of free hydrochloric acid.

In testing solutions which have been obtained by the use of *aqua regia*, special care should be taken to guard against the possible presence of free chlorine or of nitrous acid. The latter not only reduces gold solutions but gives a yellow colour with ortho-tolidine. Any reagents used should always be tested for reducing impurities; thus, on one occasion a sample of "pure" ammonium chloride completely reduced a weak gold solution.

In presence of much copper a green colour is obtained instead of a pure yellow; colorimetric comparison can, however, still be made if the standard gold solution is tinted with copper to a similar extent.—*Analyst*, xliv., No. 516.

* Read at the meeting of the Society of Public Analysts, February 5, 1919.

THE PRODUCTION OF NITROGEN COMPOUNDS.*

By JACK P. MONTGOMERY, Department Chemistry and Chemical Engineering, University of Alabama.

It is the purpose of this paper to review the sources of nitrogen compounds, and the processes of utilising them, which are being employed to successfully meet, and in many directions more than meet, the unavoidable waste of nitrogenous material.

The most important of the compounds of nitrogen by the production of which the nitrogen equilibrium may be restored are nitrogenous organic compounds produced in agriculture, ammonia and ammonium salts, nitric acid, nitrates, and oxides of nitrogen. The sources from which these compounds may be derived are the sodium nitrate deposits of Chile, bituminous coal, various by-products of food production such as cotton-seed meal and the "tankage" from packing houses, and, of late, atmospheric nitrogen.

The production of nitrogenous organic compounds in agriculture depends upon the use of a fertilising material containing available nitrogen, or compounds which may become available in the soil, or upon the direct utilisation of the nitrogen of the atmosphere in the growth of the plant. The use of seed meals and of tankage as fertilisers is becoming less each year as these materials are being used more and more as feed stuffs. This makes it increasingly necessary that such nitrogenous materials as ammonium salts and nitrates be used, or that atmospheric nitrogen be made available. The direct utilisation of atmospheric nitrogen by plants or other living organisms appears to be possible *only in* the *symbiosis of* certain bacteria upon the roots of leguminous plants. The bacteria are able to convert the atmospheric nitrogen into compounds available for themselves and to store up in nodules upon the roots of the peas, beans, clover, or vetch reserve supplies of nitrogenous materials more tham ample for the growing needs of the plant. These nodules remaining in the soil undergo the same kind of change as would other organic nitrogenous matter, and are transformed into ammonium salts or nitrates which may be utilised by following crops. This is the oldest and by far the most important of the methods for the fixation of atmospheric nitrogen. Obviously no figures are obtainable, but it is easily conceivable that under proper agricultural control this one method is capable of making good all the nitrogen waste which is normal to times of peace. The chief objection to this natural method for the fixation of nitrogen is that it requires time. The artificial methods for the fixation of atmospheric nitrogen into ammonia and nitric acid or ammonium salts and nitrates appeal more to the imagination and have of late received more attention, but we will do well not to forget this very important agricultural method.

There are two well-defined processes for making ammonia from atmospheric nitrogen, the synthetic or direct process, and the cyanamide or indirect process. Many attempts had been made to directly combine nitrogen and hydrogen, by sparking a mixture of the two gases, by heating with a catalyst, and so on, before the present synthetic process was developed by Haber and his associates. The success of the Haber process is due to great technical development accompanied by close attention to theoretical considerations.

Nernst made an exhaustive study of the equilibrium conditions in the system—

$$N_2 + 3H_2 \rightleftarrows 2NH_3,$$

and found that a higher pressure results in a greater ammonia concentration, and that certain catalytic agents favoured the forward action. Haber, by a careful development of the work of Nernst, found the most favour-

* *Chemical Engineer*, xxvii., No. 2.

able temperature and pressure conditions, and used, at first, osmium as a catalyst. This process was developed in Germany by the Badische Anilin und Soda Fabrik, a corporation which was highly subsidised by the Government. As far as has been revealed this process is known to take place in a cylindrical reaction chamber surrounded by an electrical heating resistance. The catalyst used now is probably a cheaper one than osmium. This is put into the reaction chamber, which is maintained at a temperature of 500° C. Nitrogen, obtained by the fractional distillation of liquid air, and hydrogen, made by the action of steam on iron at 300° C., are mixed in the proportion of one volume of the former to three of the latter, compressed to 200 or 225 atmospheres, and passed through the reaction cylinder. About 8 per cent of the materials present are converted into ammonia. This must be constantly removed or the reaction will come to a halt by the establishment of equilibrium in the system—

$$N_2+3H_2 \rightleftarrows 2NH_2.$$

The ammonia is removed by passing the mixed gases through a condenser where the ammonia is liquefied and removed, the remaining nitrogen and hydrogen being continually worked over with fresh supplies added from time to time.

The development of this process is believed to have a very great bearing upon Germany's ability to supply herself with munitions of war. Ammonia made by this process is converted into nitric oxide and nitrogen peroxide, by a process to be described presently, and these in turn are made into nitric acid and nitrates.

A synthetic process developed by the General Chemical Company, a process believed to be a modification of the Haber process, will be used at the Nitrate Plant No. 1 at Muscle Shoals. In this plant a part of the ammonia will be oxidised to nitric acid, and the remainder will be combined with the acid in the formation of ammonium nitrate. While this is as yet an experimental plant, it is expected that the production will be large and that other plants of the same kind will be established at other points. Although this is a "war plant," it is expected that the product will be available for use as fertilising material. This process is expected to furnish ammonium nitrate at a lower cost than is possible with any other process, and we are awaiting the outcome of the experiment with great interest.

Indirect Method First Tried.

While the Haber process is of great theoretical and practical interest it must be remembered that the indirect or cyanamide process was the pioneer method for making ammonia from atmospheric nitrogen. Frank and Caro sought to make cyanide for gold extraction, obtaining the nitrogen from the air. Although not directly succeeding in this, they worked out a process the main feature of which was a method of fixing atmospheric nitrogen in a compound, calcium cyanamide, which in turn can be used in the manufacture of ammonia. In the cyanamide method calcium carbide, with the manufacture of which you are familiar, is treated in an electric oven with atmospheric nitrogen. About three-quarters of a ton of carbide is treated per oven, and the reaction is started by using the oven as a sort of resistance furnace, the charge of carbide being employed as the core offering resistance to the current. After a temperature of about 1000° C. is reached the reaction, being exothermic, proceeds to completion according to the equation—

$$CaC_2+N_2 \rightarrow CaCN_2+C.$$

After cooling, the cyanamide charge is crushed and any residual carbide is removed by careful hydration. The ammonia is then produced by treatment with steam in an autoclave. About four tons of cyanamide are charged into the autoclave containing a dilute caustic soda solution. Steam is admitted to the autoclave, and a pressure of 200 to 250 pounds maintained for some hours. The steam and cyanamide react according to the equation—

$$CaCN_2+3H_2O \rightarrow CaCO_3+2NH_3.$$

When the autoclave valves are opened the escaping gas is about one-fourth ammonia and three-fourths steam. The mixed gases are passed into condensers and the water and ammonia separated. The nitrogen for this process, as for the synthetic process, is made by the fractional distillation of liquid air.

The Nitrate Plant No. 2 at Muscle Shoals, just been completed by the Air Nitrates Corporation, will employ this process. This plant consists of a series of factories for the manufacture of lime, carbide, liquid air, cyanamite, ammonia, and nitric acid, the latter being made by the oxidation of the ammonia. The building of this immense fixation plant has challenged the attention of the whole country because of the rapidity of the construction of such an excellent and complete series of factories, any one of which would reflect great credit upon those undertaking such a task. While this plant is a monument to American efficiency in engineering, it remains to be seen whether or not, with the country on a peace basis, it will be required or whether it can be made to pay. It should be said, however, that this is by no means an experimental plant. Every process has been well tried out, and its success or failure will depend entirely upon economic conditions of cost of materials and labour and selling price of the product. This plant will have a rated capacity of 2,000,000 pounds of nitric acid per day. The only question is, can we in piping times of peace use all of it?

Ammonia produced by these methods is usually spoken of as being an artificial nitrogen product as distinguished from the ammonia from the "natural" source, coal. Until a year or two ago, when the artificial methods of producing ammonia overtook it, the production of ammonia and ammonium salts in connection with the by-product distillation of coal was the most important source of nitrogen with the exception of the sodium nitrate from Chile, which was, and still is, the most important source. During the period from 1914 to November, 1918, so far as obtainable figures show, the production of by-product and gasworks ammonia increased only 16 per cent. Of this increase Germany is to be credited with the greatest contribution. The relatively small increase in America and the lack of any increase at all in Great Britain was no doubt due to the fact that a by-product coal distilling plant requires such a considerable expenditure of capital and such an outlay of structural material that developments along this line were not to be undertaken during the war. But the potentialities of ammonia from this natural source are very great. At present comparatively little of our American coke is being produced in by-product ovens. As more and more of the beehive ovens are replaced by the by-product plants this source of ammonia will attain greater relative prominence because of its cheapness. By-product distillation of coal is, as an industry in this country, still in its infancy, and even though we marvel at the present feats of our engineers in that line, another decade will see these very wonders eclipsed. With the great development along this line which is bound to come, stimulated, we trust, by the lusty growth of the American dye industry, we may expect to see coal rank as a highly important source of nitrogen and outstrip in pounds produced not only ammonia by fixation but the nitric acid from sodium nitrate.

Even now it appears to some of us that if the same amount of constructive energy had been directed to the development of by-product coke plants in this country as has been devoted to the development of fixations plants we would be farther along the road of preparedness. We could have gone just as far in solving our nitrogen problems and would at the same time have saved much valuable material that has gone to waste in the beehive ovens. We might have learned a great deal by paying attention to the by-product situation in Germany. In

1910 Germany was producing 400,000 tons of ammonium sulphate, a little more than one-third of the entire world production. While accurate figures since the war began are not to be had, it is known that the by-product coke industry in Germany has greatly expanded, and there is reason to believe that they had reached an annual production of 1,000,000 tons of ammonium sulphate, or about one-half of the world's production, by the middle of the present year. Much of this material was used in the manufacture of munitions, and Germany did not have to depend too largely upon artificial nitrogen compounds.

(To be continued).

SEED MIXTURES FOR LAND AFFECTED BY CLOVER SICKNESS.*

Owing to the high cost of nitrogenous fertilisers, farmers should endeavour to conserve nitrogen by every means possible. Leguminous plants should therefore take a prominent place in every rotation. It is well known that in many districts red clover is liable to become "clover sick" if sown on the same field at too short intervals. It is probable that none of the leguminous forage plants are absolutely safe from attacks of "clover sickness," but it is evident that red clover is the most susceptible. Peas or beans, both valuable crops under existing conditions, could with advantage be introduced into the rotation on land that is known to be "sick" provided that it is at the same time suitable for the production of these crops, while in the formation of rotation leys, plants other than red clover should be used on "sick" land; or a mixture consisting only partially of red clover should replace large seedings of red clover by itself. Alsike clover, white clover, and trefoil do not suffer from "clover sickness" to nearly the same extent as red clover, and may therefore be used as substitutes for red clover.

Moreover, there is reason to believe that English-grown late-flowering red clover in particular and also broad red clover, from seed harvested in England, are less susceptible to "clover sickness" than imported clover. When, therefore, red clover is used at all in mixtures for "sick" land it is desirable that every endeavour should be made to secure home-grown stocks of seed for the purpose. On (chalky) soils, or in regions of comparatively low rainfall, trefoil may be largely used, while in districts of high rainfall more reliance should be placed on Alsike clover. The following mixtures are suggested:—

One Year Leys.—

	Lbs. per acre.			Lbs. per acre.
Chalky soils or low rainfall—				
Red clover ..	4	or	Alsike clover ..	4
Alsike clover ..	6		Trefoil	12
Trefoil	6			
High rainfall—				
Red clover ..	4			
Alsike clover ..	8			

It appears also from experiments conducted in Yorkshire and from experience elsewhere that red clover grown in conjunction with rye-grass is less susceptible to sickness than when grown pure; in districts adapted for growing mixed "seeds" the clovers might be decreased to half the above quantities and half a bushel of Italian rye-grass added to the mixture.

Two Year Leys.—White clover should be more largely relied upon in mixtures for two year leys, in which mixtures both Italian and perennial rye-grasses would also take a prominent place.

	Low rainfall, lbs. per acre.	High rainfall. lbs. per acre.
Red clover	2	2
Alsike clover	3	4
White clover	2	2
Trefoil	3	—
Italian rye-grass	6	6
Perennial rye-grass.. ..	4	4

On soils where giant sainfoin (see *Leaflet* No. 280) is known to succeed, especially where it has not been grown for a number of years, this crop sown pure might usefully replace red clover on "sick" land, whilst the value of lucerne (see *Leaflet* No. 160) on soils that suit it must, in this connection, be strongly emphasised. The veitch (see *Food Production Leaflet* No. 51) is another valuable leguminous plant which, as well as providing nitrogenous residues for the benefit of subsequent crops in the rotation, has a special value at present from the point of view of adding to the diminished supplies of hay. (*Leaflet* No. 184 on red, white, and Alsike clovers may also be consulted).

London, S.W. 1, February, 1919.

* Board of Agriculture and Fisheries, *Food Production Leaflet* No. 61.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 20, 1919.

Sir J. J. Thomson, O.M., President, in the Chair.

The following papers were read:—

"*Magnetic Storms of March 7-8 and August 15-16, 1918, and their Discussion.*" Charles Chree, Sc.D., F.R.S.

The paper contains a discussion of two magnetic storms —the first on March 7-8, the second on August 15-16, 1918. For the March storm curves were utilised from Kew, Eskdalemuir, and Agincourt (Toronto) Observatories. For the August storm Kew and Eskdalemuir curves were alone available. The storms were of the same general type as one which occurred on December 16-17, 1917, and was discussed in a previous paper; but, unlike the previous storm, they both had conspicuous Sc's. ("sudden commencements"). The movements constituting the Sc. on August 15-16 were unusually large and their oscillatory character was very prominent at Agincourt and Eskdalemuir. In both cases, as in the storm of December, 1917, disturbance was much larger at Eskdalemuir than at Kew, especially in the vertical force. The declination changes at the two places showed rather a close resemblance, but the variations in the other elements differed at times not merely in amplitude, but in general character. The disturbance at Agincourt on March 7-8 was similar in intensity to that at Eskdalemuir, but conspicuously different in many details. There were some exceedingly large and rapid changes, especially of declination and horizontal force, at Agincourt, the range of the former element being about 2° 5', as compared with 51' at Kew. Some consideration is given to the resemblances and differences between these storms and some mean results for storms having Sc's. given in a recent paper by Dr. S. Chapman.

"*The Transparency of Biotite to Infra-red Radiations.*" By L. C. Martin.

The paper describes a curious reversible variation with temperature in the infra-red transmission of biotite. The infra-red apparatus employed was designed by Prof. Callendar and Mr. A. Eagle. Its optical properties are examined. Tables and curves showing the variation in transmission of biotite with wave-length at various temperatures are given and certain possible explanations are examined. The general nature of the effect is a halving of the transmission for a rise in temperature of about 200° C.

PHYSICAL SOCIETY.

Annual General Meeting, February 14, 1919.

Mr. W. R. COOPER, M.A., B.Sc., in the Chair.

IN opening the meeting the Chairman referred to the loss the Society had sustained by the death of Prof. G. Carey Foster, one of the founders, and mentioned that the President, Prof. C. H. Lees, was representing the Society at his funeral that afternoon.

The Report of the Council was read by Prof. W. Eccles.

The Report of the Treasurer was read by Mr. W. R. Cooper.

Both reports were unanimously adopted.

While the ballot papers for the election of Officers and Council were being collected and counted, votes of thanks were accorded to the Honorary Auditors, the Officers and Council, and the Governors of the Imperial College, the respective proposers and seconders being Mr. C. C. Paterson and Dr. Bryan, Prof. Fortescue and Dr. Makower, Prof. Howe and Dr. Owen.

Mr. E. H. Rayner moved and Mr. W. R. Cooper seconded a vote of thanks to Prof. W. Eccles for his past services as joint honorary secretary.

The scrutators announced the result of the election of Officers and Council for the ensuing year :—

President—Prof. C. H. Lees, D.Sc., F.R.S.

Vice-Presidents (who have filled the office of President) —Prof. R. B. Clifton, M.A., F.R.S. ; Prof. A. W. Reinold, C.B., M.A., F.R.S. ; Sir W. de W. Abney, R.E., K.C.B., D.C.L., F.R.S. ; Prin. Sir Oliver J. Lodge, D.Sc., F.R.S. ; Sir Richard Glazebrook, C.B., D.Sc., F.R.S. ; Prof. J. Perry, D.Sc., F.R.S. ; C. Chree, Sc.D., LL.D., F.R.S. ; Prof. H. L. Callendar, M.A., LL.D., F.R.S. ; Prof. A. Schuster, Ph.D., Sc.D., F.R.S. ; Sir J. J. Thomson, O.M., D.Sc., F.R.S. ; Prof. C. Vernon Boys, F.R.S.

Vice-Presidents—Prof. W. Eccles, D.Sc. ; Prof. J. W. Nicholson, M.A., D.Sc., F.R.S. ; Prof. O. W. Richardson, M.A., D.Sc., F.R.S. ; R. S. Willows, M.A., D.Sc.

Secretaries—(*Papers*) H. S. Allen, M A., D.Sc., 5, Presburg Road, New Malden ; (*Business*) F. E. Smith, O.B.E., F.R.S., National Physical Laboratory, Teddington.

Foreign Secretary—Sir Richard Glazebrook, C.B., D.Sc., F.R.S.

Treasurer—W. R. Cooper, M.A., B.Sc., 82, Victoria Street, S.W. 1.

Librarian—S. W. J. Smith, M.A., D.Sc., F.R.S., Imperial College of Science and Technology.

Other Members of Council Prof. E. H. Barton, D.Sc., F.R.S. ; Prof. W. H. Bragg, C.B.E., M.A., F.R.S. ; C. R. Darling, F.I.C. ; Prof. A. S. Eddington, M.A., M.Sc., F.R.S. ; D. Owen, D.Sc. ; Major C. E. S. Phillips, F.R.S.E. ; E. H. Rayner, M.A. ; S. Russ, D.Sc. ; T. Smith, B.A. ; F. J. W. Whipple, M.A.

After the conclusion of the general business, Prof. LEES took the Chair.

A paper entitled "*Temperature Coefficient of Tensile Strength of Water*," by S. SKINNER M.A., and R. W. BURFITT, B.Sc., was read by the latter.

The liquid is forced under pressure through a capillary constriction between two limbs of a U-tube. By trial the pressure is adjusted until the speed in the capillary is sufficient to produce rupture. This is judged by the sound and also the appearance. The whole U-tube is immersed in a bath, the temperature of which can be varied. Actual observations of rupture, velocity, and temperature are recorded up to about 100° C., from which it is deduced that the tensile strength becomes zero in the neighbourhood of 245° C., which is in agreement with theory.

DISCUSSION.

Dr. VINCENT asked what arrangements were made to get the liquid back into the virgin state after it had been

Dr. BRYAN asked how dissolved gas affected the results. In experiments by Worthington and others the water required to be very carefully boiled before it showed any tensile strength at all.

Prof. LEES also commented on the fact that the liquid experimented on here contained dissolved gas. In Worthington's experiments with gas-free water the tensile stress was about 2 atmospheres, as far as he remembered. This seemed of a different order from that obtained by the authors.

Mr. F. J. W. WHIPPLE asked where the tensile strength came into the formula. The diagram seemed to connect velocity and temperature only.

Mr. BURFITT, in reply to Dr. Vincent, said the liquid was always allowed to stand until all cloudiness had disappeared, and any dissolved gas was in equilibrium. There was no doubt the presence of dissolved gas promoted rupture. Worthington's measure was static, and there was no danger of air getting in if the liquid was initially air free. In the present method it was impossible to prevent some air becoming dissolved. With reference to Mr. Whipple's comments, the tables are not primarily intended to give actual values of the tensile stress, but to give its variation with temperature. If desired, the value of C in the theoretical formula can be calculated from the figures given.

A paper entitled "*Vector Diagrams of Some Oscillatory Circuits Used with Thermionic Tubes*," was read by Prof. W. H. ECCLES.

The method of the crank or vector diagrams used commonly in the study of alternating-current circuits is applied in the paper to the assemblage made up of an oscillator, the thermionic relay maintaining it in oscillation, and the devices linking these two parts. The diagrams then serve as substitutes for the usual treatment of the problem by differential equation, and from them may be obtained all the formulæ. They have, besides, the advantage of exhibiting to the eye the phases of the currents and voltages in every part of the circuits. In forming the diagrams the potential drop across the oscillator is calculated by the usual rules of the alternating-current diagram, and added geometrically to the potential drop across the tube. This total is made equal, in magnitude and phase, to the voltage applied at the instant to the grid multiplied by the voltage factor of the relay. In its turn the voltage applied to the relay depends upon and is obtained from the current running in a portion of the oscillator. The fitting together of these lines gives all the conditions to be satisfied for the maintenance of steady oscillations.

DISCUSSION.

Prof. G. W. O. HOWE agreed that you could not really understand the conditions in a circuit unless you were able to put down the currents and voltages in a vector diagram. He had attempted himself to simplify Vallauri's treatment for students, but without as much success as Dr. Eccles. He had usually looked at these circuits from this point of view : The oscillatory circuit apart from the valve has a certain equivalent resistance. To maintain oscillations the equivalent of a negative resistance must be introduced. There are two ways of varying the current in the bulbs ; the P.D. on the terminals or on the grid may be varied. In the latter case the current may be increased even if the total P.D. on the bulb is diminished, and if this condition can be arrived at we have the equivalent of a negative resistance to the oscillations. You have to arrange a coupling device so that the variations of current in the plate circuit produces suitable variations of potential of the grid. From the characteristic of the plate circuit you can determine the critical value of the mutual inductance between plate and grid circuits to give the equivalent negative resistance necessary for maintenance of steady oscillations.

Prof. C. R. FORTESCUE said the method of approach

as a generator of an E.M.F., gEg, enables a voltage am to be plotted instead of the more usual current am. This is an undoubted advance, and simplifies nal adjustment of the diagram to suit the conditions ie tube and circuit. At various times many vector ams have been drawn for various oscillatory circuits; n the whole the results have hardly come up to ex- itions. There appears to be three reasons for this, (*a*) In order to draw the diagram at all a very clear ht into the conditions is required. In other words, necessary to know the final result before the diagram mpleted. In the diagram of Fig. 3 of the paper it is ssary to know, firstly, that the angle θ is a positive e, and, secondly, that the effective E.M.F. of the is in phase with the voltage applied to the grid. The r condition is, of course, obvious from the action of ube, but the former is by no means obvious, and has discovered by trial and error. If, for example, the ent I is considered to be flowing through the induc- e, then θ must be taken as an angle of lag, as will be d if an attempt is made to plot out this diagram. (*b*) quantities are such that it is impracticable to plot the rams to scale. For example, if the numerical values ie first example on page 3 are taken, the ratio of the th of the line OUg of Fig. 3, to the length DQ is of order of 1 to 500,000. Actually, if Fig. 3 is plotted to e, it becomes a diagram vertically up and down the d. (*c*) Finally, there is the common experience of the difficulty in drawing the diagrams. There are many ibilities of confusion with the ordinary current diagram, it is possible that with the author's voltage diagram e troubles will be very much reduced. It would appear the true function of these diagrams, when numerical es are applied or when the diagrams are drawn to e, is to justify the practical method commonly used of rding the valve as a power supply. The anode ent is in phase with the voltage across the oscillatory uit. Taking the alternating components only, the luct of the anode current and the circuit voltage gives power supplied to the circuit. The anode current ends upon the anode and grid voltages, *i.e.*,

$$i = h_a e_a + h_g e_g,$$

iven on page 1 of the proof of this paper. To within nall percentage this power is absorbed by the circuit es. If R+S is the effective resistance of the oscillatory uit, then for the oscillations to be maintained or built the power supply from the valve must be equal to or iter than the $J^2(R+S)$ loss. This method of dealing the problem has many practical advantages, and has n in use for some years. Hazeltine has described, in "Proceedings" of the American Institute of Radio gineers, the application of the method to various uits, notably the circuit in which a condenser is con- ted across the grid inductance h. It is very well known the author of this paper has had experience of many er circuits and applications of three electrode relays, it is to be hoped that he may be able to give to the iety further papers on this same subject. In particular, ector treatment of the De Forest ultraudion circuit ild be of great interest, as this circuit is one which has sented very great difficulties when any attempts have n made to calculate the condition for instability.

Ir. J. NICOL asked if there was any lag between the age applied to the grid and the effect on the current in valve.

r. D. OWEN said it was assumed that the action of the e was an amplification of voltage. Actually what pened was a variation in the resistance of the valve. eemed rather remarkable that this should be regarded voltage effect. He did not like Prof. Howe's idea of gative resistance, as such a conception had no physical ificance. A negative value of dV/dC was by no means same thing as a negative value of V/C, which would equired before we could talk of a negative resistance. the author find it satisfactory to treat the quantity s a constant?

Mr. F. E. SMITH thought the paper of great value. He agreed with Prof. Fortescue that a great amount of inter- esting work was still to be done in connection with these problems.

Capt. TURNER referred to a sentence occurring in the section dealing with a particular case: "It is noteworthy that . . . no resistance." This seemed to imply that an infinitesimal change in E would produce a finite change in the steady component of the anode current.

Dr. ECCLES, in reply, said that he did not think vector diagrams were ever used quantitatively. They were mainly used to derive a formula, and the scale of the vectors was immaterial. As regards lag, he was not aware of any definite knowledge on this point, but the fact that nowadays waves of 30,000,000 per second were obtained showed that the lag must be very small. He thought it was justifiable to assume it zero in slow circuits. The conception of the valve as a voltage amplifier seemed a difficulty; but if we vary the resistance of one part of a circuit containing a fixed E.M.F it is clear that the P.D. on the remainder of the circuit will also vary; so that the varying resistance can be regarded as a source of varying E.M.F. applied to the remainder of the circuit. The quantity h_a was not constant. As regards Capt. Turner's point, he was referring here to a case in which there was no resistance in the inductance circuit.

A paper entitled "*A Small Direct-current Motor Using Thermionic Tubes instead of Sliding Contacts*," by Prof. W. H. ECCLES and Mr. F. W. JORDAN, was read by the latter.

In this motor the rotating part is an ebonite disc with iron teeth on its periphery, and the stationary part com- prises two electromagnets with their poles close to two teeth. One electromagnet is connected to the grid of a thermionic relay, the other is included in the plate circuit. When during rotation a tooth passing the grid magnet induces a voltage in its winding the consequent transient increase of current through the other magnet causes this magnet to exert a pull on the tooth ap- proaching it. We thus have a small motor without commutator or spark which may under no-load be driven up to a speed of 4000 to 6000 revs. per min. from the lighting supply.

Ordinary Meeting, February 28, 1919.

Prof. C. H. LEES, President, in the Chair.

A PAPER "*On Simplified Inductance Calculations, with Special Reference to Thick Coils*," by Mr. P. R. COURSEY, was read, in the absence of the author, by Mr. J. NICOL.

The method of calculation advocated in the paper is based on an extension of Nagaoka's formula for single layer coils, to include as well all ordinary forms of thick coils. Rosa's formula for thick coils is put into the same form as Nagaoka's, and its use enables a series of correc- tion factors to be calculated for various coil thicknesses. By the aid of a single sheet of curves giving values of these correction factors the inductance of any form of coil likely to be met with in practice may be readily calculated, using only one simple standard formula for all cases. Reasonable accuracy is obtained even in the limiting example of a single turn of wire. The results arrived at agree well with other published charts, which are usually of more limited application, while the use of a single formula for all cases lessens the liability to error.

It is also shown that Raleigh and Niven's formula enables the calculation of the correction factors for very short coils to be carried out without having recourse to Nagaoka's more complicated expressions.

DISCUSSION.

Dr. ECCLES said that as the author had mentioned an abac given in the speaker's book on "Wireless Tele- graphy," it was well to remark, first, that this abac was

deliberately made of its present range so as to provide an open scale for coils of the proportions used in practice. For the rare cases of coils outside the range of the abac very simple formulæ are available. Dr. Russell's formulæ were used in making the abac, because they seemed more convenient for the purpose than the results of Nagaoka, to which they were, of course, equivalent. By constructing new curves for dealing with coils of several layers the author has rendered a great service, and has opened easy paths though a forest of laborious theoretical calculation. Now that this has been done it will be much easier to compare the measured values obtained on actual coils with the calculated values, and so we shall be aided to accumulate experience of the effects of high frequency eddy currents on the inductance of coils.

Prof. HOWE agreed with Prof. Eccles' remark about the general utility of Mr. Coursey's investigation. The chief differences between the author's curves and those of the Bureau of Standards was that in the latter the ratio D/l and k, which was a function of D/l, were combined into a single function.

Mr. NICOL, in reply, referred to formulæ published in the *Electrician* by Mr. Coursey a few years ago, and considered that the step now taken, which resulted in restricting the values of k to between 0 and 1, combined with the general inclination of the curves to about 45 deg. with the axis, gave much greater convenience in reading.

A Demonstration of Some Acoustic Experiments in Connection with Whistles and Flutes was given by Dr. R. DUNSTAN.

Experiments were made with hollow spheres, cylinders, and cones with holes of various sizes and in various positions. Bernoulli's theorem, which gives the wave-length of the sound produced by a cylindrical pipe in terms of the length of the pipe and an end-correction depending on the diameter only, was shown to be quite inadequate for practical purposes, the pitch depending on many other factors, such as the wind pressure, the size and shape of the blow-hole, &c. Cylindrical flutes appear to require an end-correction which—within certain limits—is equal to D^2/d, where D is the diameter of the pipe and d the mean diameter of the mouth hole (which is often oval in shape). In the shortest flute experimented with, which was only half an inch long, Bernoulli's theorem would give the wave-length as two inches, whereas it was actually fourteen inches.

The conclusions drawn from the experiments are that in blowing across a hole in a hollow body a force existed on an elastic substance. The result is a "*spring back*," which produces an aerial throb, puff, or pulsation. The frequency of the pulsation is determined by relations between the dimensions of the instrument, the size of the hole, the wind pressure, &c. Any resulting sound has its wave-length determined by the frequency and not *primarily* by the dimensions of the instrument, as in the usual text-book treatment.

DISCUSSION.

Prof. BRAGG referred to Lord Rayleigh's work on open pipes and flasks, and said that since the internal pressure of the air would vary with the size of the aperture it was easily conceivable that a difference of pitch would result when a change was made in the size of the aperture.

Mr. F. J. W. WHIPPLE outlined Lord Rayleigh's explanation of the long wave-length of the notes obtained from a hollow sphere.

Mr. T. SMITH asked if the variation in pitch with the position of the hole along the cylinder had been fitted to a formula—for instance, was the change in pitch proportional to the square of the distance of the hole from the centre of the cylinder?

Mr. NICOL spoke of the end correction, and stated that students often applied the correction to the *closed* end of pipes, which was incorrect.

Mr. F. E. SMITH said the end correction was useful in electrical problems, and gave an illustration of the variation of D^2/d in an electrical case.

The PRESIDENT asked if there was much variation in the ratio D/d, and said he thought the formula was important if it could be verified over a wide range. He referred to Lord Rayleigh's experiments on flasks as closely analogous to those of Dr. Dunstan.

In reply, Dr. DUNSTAN stated that the range of D/d was not very large in the instruments he had used.

A Demonstration of a new Polariser was given by Mr. G. BRODSKY.

In the course of experiments with polarisers built of piles of glass plates disadvantages due to bulkiness of the apparatus and loss of light had to be overcome.

The idea occurred to him to place the pile of plates between two prisms of the same glass in such a manner as to—

(*a*) Reduce the length of the polariser by one-half;
(*b*) Utilise the full aperture of the pile; and
(*c*) To get rid of *all* reflected light.

Results obtained with experimental prisms he showed were so good that they could be considered a very fair substitute for Nicol prisms of corresponding size, and the very small amount of light escaping through crossed prisms (which could be reduced further by additional plates) is for most purposes negligible.

There would be no difficulty in building such polarisers to any required size, as all the material consisted entirely of glass in unlimited quantities and at reasonable price, and it was hoped that this invention (Brit. Patent 121,906) would be used for many purposes.

Polarisers for directly transmitted light were hitherto very scarce and costly, so that many uses they could be put to remained undeveloped (such as stereoscopic kinematography).

The new polariser could also be adapted to advantage in microscopes, saccharimeters, optical pyrometers, &c., and used for optical benches in the lecture room.

Experiments with piles of glass plates showed a very large discrepancy between the calculated and observed angle for best extinction. Whatever the glass used, and whatever the quality of the surface, this discrepancy came consistently to some 10 deg., whereas thin microscope cover plates were found to be useless.

There seemed to be still an interesting field for investigation as to the conditions affecting the surface of glass plates used in polarisers.

DISCUSSION.

Mr. T. SMITH said it was difficult to discuss the merits of various forms of polariser, as many forms had been proposed and much was of a confidential character. He had been struck by the presence of two opposite tendencies in constructing such apparatus. In one group the optical portions of the apparatus were made large, and efforts were directed to increasing the size; in the other group, where the attainment of the same ultimate object was in view, these parts were made as small as possible.

The PRESIDENT asked if it was not possible to get equally good results without prisms by reflection only. He thought prisms made the arrangement complicated.

Mr. BRODSKY, in reply, explained that he agreed with the remarks about reflection, but that his efforts were confined to transmission effects for a particular purpose.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 5, 1919.

Dr. SAMUEL RIDEAL, President, in the Chair.

A CERTIFICATE was read for the first time in favour of Mr. Madanlal Jekisandas Gajjar, M.A. (Bombay), and Mr. James Sorley, F.I.C.

Certificates were read for the second time in favour of Messrs. Robert Odell Bishop, A.I.C.; Hubert William Bywaters, D.Sc., F.I.C., Ph.D.; B. S. Evans, M.C.,

B.Sc.Lond., F.I.C.; F. S. Fowweather, M.Sc., A.I.C.; Robert Atkinson Oddy; W. B. Pollard; Charles Kenneth Tinkler, D Sc., F.I.C.

Mr. Cecil William Wood was elected a Member of the Society.

The following papers were read:—

"*Approximate Method of Analysis of Sausages and Meat Paste.*" By Geo. Stubbs, O.B.E., F.I.C., and A. More, A.R.C.S., F.I.C.

The determination of moisture, fat, proteins, and ash is carried out in the usual manner, and the proportion of carbohydrates taken by difference. The estimation of lean meat is based on the absence of carbohydrates in meat and the amount of proteins in the cereal products used as fillers.

"*Method for the Determination of Small Quantities of Acetone, Alcohol, and Benzene in the Air.*" By Major S. Elliott, B.Sc., F.I.C., and Capt. J. Dalton, M.C.

A measured quantity of the air is drawn through suitable apparatus, the vapours being absorbed simultaneously as follows:—The acetone in alkaline iodine solution and the excess of iodine titrated with thiosulphate. The alcohol in dilute chromic acid and, after oxidation to acetic acid, the excess of chromic acid is titrated with iodine. The benzene in a mixture of conc. sulphuric acid and fuming nitric acid, converted into dinitro-benzene, and after extraction with ether, reduced by a known excess of stannous chloride and the excess of the last reagent titrated with iodine.

"*Analysis of Sausages, Meat Pastes, and Army Rations.*" By A. W. Stokes, F.I.C.

The Food Control authorities limited the percentage of meat which might be contained in sausages to be sold at a given price, but did not limit the quantities of bread, water, and fat. The desirability of limiting the quantities of water, bread, and fat was shown by a particular sample which contained about equal parts of added water, bread, fat, and meat. Since meat contains 70 per cent of water and bread 40 per cent, no added water should be allowed. In the United States the use of bread in sausages is prohibited, and, as the bread is often soaked in water before use, thereby increasing the percentage in the finished product, the author points out that this prohibition might with advantage be enforced in England.

INSTITUTE OF CHEMISTRY.

The London and South-Eastern Section of the Institute of Chemistry was formed at a meeting held at 30, Russell Square, on March 14.

Sir Herbert Jackson, President, in opening the proceedings, said that the Local Sections of the Institute recently formed in various parts of the country had already demonstrated their usefulness, and were taking an active part in assisting the Council in promoting the interests of the profession of chemistry. The Council desired that the Local Sections should have a free hand in the conduct of their business. The President, therefore, called upon the members to elect a Chairman for the meeting.

Dr. Bernard Dyer having been elected to the chair, the Section was declared duly formed.

A Committee was elected as follows:—Mr. C. T. Abell, Dr. O. L. Brady, Mr. A. J. Chapman, Miss E. M. Chatt, Dr. Bernard Dyer, Mr. A. V. Elsden, Mr. Norman Evers, Mr. J. A. Gardner, Mr. C. S. Garland, Dr. W. H. Gibson, Mr. W. H. Harrison, Mr. E. M. Hawkins, Prof. J. W. Hinchley, Prof. P. H. Kirkaldy, Mr. E. H. Lees, Mr. T. Macara, Mr. W. A. C. Newman, Mr. F. M. Potter, Mr. F. M. Ray, and Mr. J. Miln Thomson.

Mr. William Bacon was appointed Hon. Secretary, *pro tem.*

The draft rules for Local Sections were provisionally adopted, and a general discussion ensued on the proposed revision of the By-Laws for the election of the Council of the Institute.

CORRESPONDENCE.

ATOMIC STRUCTURE AND CHEMICAL AFFINITY.

To the Editor of the Chemical News.

Sir,—Referring to my article, entitled as above, in last week's issue of the Chemical News, may I claim a little more space to correct two mathematical errors?

Page 145, left-hand column, bottom line, "10^{-2} cm." should read 10^{-24} cm.

Page 149, left-hand column, first figures in table, "10^{-6}" should read 10^{6}.

It will be seen that by making this latter correction the gradation of the wave-lengths is as it should be.—I am, &c.,

F. H. L.

DYEING EXPERIMENT.

To the Editor of the Chemical News.

Sir,—Turning over the pages of my laboratory notebooks for the late sixties, I find the following:—"Take half a grm. of a mixture in powder of potassium methyl sulphate and potassium iodide, tint *slightly* with rosaniline, moisten with glycerin, and warm carefully over the flame; Hofmann's violet is formed. On addition of water, silk or wool can be dyed in the solution. The experiment would serve for lecture demonstration when dealing with aniline dyes. Glycerin retains the CH_3I."

The enclosed was dyed by this means. [*The strip of silk accompanying was dyed a pleasing shade of violet.*—Ed.]—I am, &c.,

Experimenter.

MISCELLANEOUS.

Institute of Chemistry.—At a meeting of Fellows and Associates of the Institute of Chemistry held at Milburn House Café, Newcastle-upon-Tyne, it was decided to form a Local (Newcastle and North-East Coast) Section. Prof. P. Phillips Bedson presided, and the Registrar of the Institute was also present. A Committee was appointed consisting of Pro. Bedson, Dr. J. T. Dunn, Prof. Henry Louis, Mr. R. A. Moore, Mr. C. H. Ridsdale, and Mr. Thomas Wallace. The Committee was empowered to add three to their number, and Dr. Dunn was appointed Hon. Secretary *pro tem.* The draft rules for Local Sections of the Institute were discussed and approved, as was also the suggested scheme for the revision of the By-laws for the election of the Council of the Institute.

MEETINGS FOR THE WEEK.

Monday, 7th.—Royal Institution, 5. (General Meeting).
— Royal Society of Arts, 4.30. (Cantor Lectures). "Problems of Food and their connection with Our Economic Policy," by Prof. H. E. Armstrong.
— Society of Chemical Industry, 8. "Drying by Heat in conjunction with Mechanical Agitation and Spreading," by E. A. Alliott. "Estimation of Carbon Disulphide—a Critical Examination of the various Methods usually Employed," by P. E. Spielmann and F. B. Jones. "Estimation of Thiophene," by P. E. Spielmann and S. P. Schotz. "Estimation of 'Free Carbon' in Tar and Pitch," by P. E. Spielmann and H. Wood.

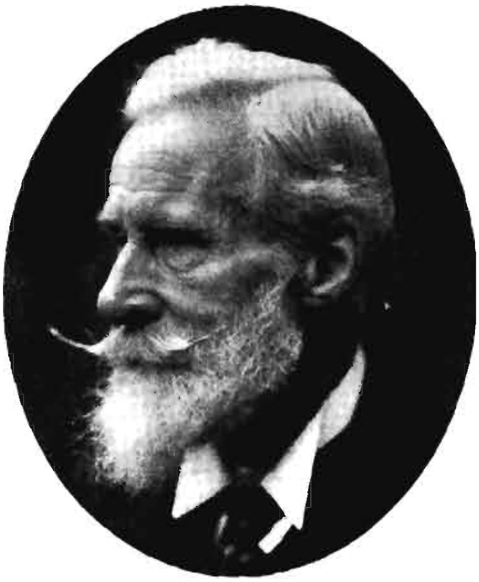
Tuesday, 8th.—Royal Institution, 3. "British Ethnology—The People of Wales," by Prof. A. Keith.

Wednesday, 9th.—Royal Society of Arts, 4.30. "Housing and Infant Mortality," by Dr. L. E. Hill.

Thursday, 10th.—Royal Institution, 3. "Colloidal Matter and its Properties," by Prof. A. Findlay.
— Institution of Electrical Engineers, 6. "Notes on Surface Condensing Plants, with Special Reference to the Requirements of Large Power Stations," by R. J. Kaula.

Friday, 11th.—Royal Institution, 5.30. "Piezo Electricity and its Applications," by Prof. Sir J. J. Thomson.

Saturday, 12th.—Royal Institution, 3. "Spectrum Analysis and its Application to Atomic Structure," by Prof. Sir J. J. Thomson, O.M.



SIR WILLIAM CROOKES, O.M., F.R.S.,

Born June, 1832. Died April, 1919.

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SIR WILLIAM CROOKES.

THE death of Sir William Crookes, which took place on Friday morning last, has been announced the world over, and full accounts of his labours and attainments have been published. There is no need for repetition in these pages; but a few words from one who for more than half a lifetime has been closely associated with him in his scientific work may not be considered out of place.

Sir William Crookes was a remarkable man: scientific work was his chief object in life; research and the progress of science his one interest.

His energy and patience were remarkable, both in success and failure—for of failures there were many about which the world knew nothing.

There were two terms that he called "bad words," and would not allow in the laboratory —one was "cannot," the other "near enough."

He was a hard worker; day in day out was filled with labour; and one of his common sayings was that a man could not be really happy unless he had just a little more to do each day than he could possibly finish.

The work of the CHEMICAL NEWS was one of his few recreations, and the paper was under his personal control from the day of its foundation in 1859 until within a few weeks of his death.

The death of Lady Crookes, which took place in May, 1916, deprived him of his one companion, and undoubtedly hastened his death. With her he lost his main interest in life, and, although he bravely fought on, it was plain to see that he would never be the same again. Gradually his strength gave way, and the writer, watching him, saw a daily added feebleness; but there was never a murmur or word of complaint, always the same kindly greeting and pleasant smile, until physical weakness gained the upper hand and he passed quietly away in the early hours of the morning.

"And so familiar landmarks disappear, old memories fade away, and all the busy actors in life's theatre vanish, and those who are left are those who are to be pitied."

THE CHEMICAL NEWS

VOL. CXVIII., No. 3078.

A STUDY OF THE PREPARATION OF CERTAIN ORGANIC SALTS OF TELLURIUM.*

By AARON M. HAGEMAN.

IN an investigation described elsewhere (*Journ. Am. Chem. Soc.*, 1919, xli., 300) it was necessary to secure solutions of tellurium in a number of non-aqueous solvents. This led to an investigation of certain organic salts of tellurium, since, in many cases, combinations of a metal with an organic acid radical are more likely to be dissolved by organic liquids than are inorganic salts. Although tellurium dioxide is chiefly acid in character, there are numerous cases where it shows specific basic tendencies. This suggested a general method for the preparation of organic salts of tellurium, namely, the treatment of tellurium dioxide with the free organic acid. In some cases this proved to be a satisfactory method of preparation, while in numerous other cases a chemical union could not be brought about by this means. This was especially true where the acid character of the organic acid was unusually weak.

* Abstract of part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xli, No 3.

Experimental.

Tellurium Acid Tartrate.—It was known to Berzelius (*Pogg. Ann.*, 1826, viii., 411) that tellurium dioxide could be dissolved in tartaric acid and a salt separated out in which tellurium acted as a base. Becker further studied this reaction and reported (*Ann.*, 1876, clxxx., 257) that if a solution of tellurium dioxide in tartaric acid was allowed to evaporate spontaneously in the air, long, radiating, colourless crystals separated out, which his analysis showed to be tellurium acid tartrate, $Te(HC_4H_4O_6)_4$. Becker (*loc. cit.*) states it is very difficult to separate these crystals from the tartaric acid itself.

In the present work the preparation of the salt consisted in treating a solution of tartaric acid, saturated at 20° C., with an excess of purified tellurium dioxide which had been ground to pass a 200-mesh sieve. The mixture was contained in an Erlenmeyer flask fitted with a one-holed rubber stopper in order to minimise evaporation and was heated in a sand-bath at a temperature of 70° C. At the end of three days, reaction had taken place, as evidenced by a decrease in the quantity of the dioxide, while a small amount of elementary tellurium had separated out.

After prolonged heating at this temperature, a portion of the liquid was filtered and the materials in solution

allowed to crystallise. After being freed from the mother-liquor as completely as possible by pressing between filter-paper, an analysis of the colourless crystals showed them to contain 5·60 per cent tellurium. The formula $Te(HC_4H_4O_6)_4$ requires 17·62 per cent cent tellurium. The flask containing the dioxide and tartaric acid was heated again for two months longer at 70° C. and crystallisation allowed to take place at room temperature, since if the solution is boiled the tellurium will slowly but completely precipitate as the element. The crystals separating out proved to contain 16·38 per cent tellurium, which is approximately the theoretical percentage required.

The reaction taking place between tellurium dioxide and tartaric acid may be summarised as follows:—A strong solution of tartaric acid slowly dissolves tellurium dioxide with the formation of tellurium acid tartrate. Inasmuch as the solubility of the free acid and newly formed salt are very nearly the same, it is impossible to separate them by this means. It consequently becomes necessary to continue the reaction to completion. Heating accelerates the reaction, but a boiling temperature must be avoided as it will cause the separation of tellurium in the elementary form.

Tellurium Acid Citrate.—Since tellurium was able to replace one of the two hydrogen atoms of the dibasic tartaric acid, it was interesting to determine the number of hydrogen atoms this element was able to replace in a tribasic organic acid. Preliminary experiments showed tellurium dioxide to be slowly dissolved by citric acid. Tellurium dioxide and a solution of citric acid were heated together for one month in a manner similar to the procedure just described. During this time no elementary tellurium was set free as in the case with tartaric acid. Crystals separating out from the supernatant liquid after concentration on a hot plate were of two different types. They consisted of large, colourless crystals which were recognised as crystals of citric acid, and some small white opaque crystals. An analysis of the latter showed a content of 9·73 per cent tellurium. By dissolving the small, white, opaque crystals in distilled water and recrystallising, it was found that similar crystals separated first and others of citric acid later. An analysis of the former showed them to contain 21·25 per cent tellurium. Fractional crystallisation was therefore continued. The results of the analyses carried out with each fraction of crystals are arranged in the accompanying table:—

Fraction.	Wt. sample. Grm.	Wt. Te found. Grm.	Te. Per cent.
1.	0·6133	0·0509	9·73
2.	0·5270	0·1120	21·25
3.	0·5793	0·1394	24·07
4.	0·5439	0·1333	24·50
5.	0·3264	0·0819	25·09

Since the percentage of tellurium required for the formula $Te(HC_6H_5O_7)_2$ is 25·10 per cent, it appears that this compound is produced by the action of citric acid on tellurium dioxide. Tellurium acid citrate may be described as a white, opaque, finely crystalline compound which tends to separate in small, radiating clusters. In comparing its preparation with that of the acid tartrate, it is of interest to note that its solution in water will withstand boiling temperatures without reduction to the element. Its solubility is sufficiently less than that of citric acid to permit its complete separation from the free acid.

Tellurium Oxalate.—If tellurium dioxide is heated with a saturated solution of oxalic acid, a certain amount of tellurium is held in solution as shown by tests for the element. If such a solution is allowed to crystallise spontaneously in the air, a mixture of crystals of the dioxide and acid separate. There seems, therefore, to be no compound existing between tellurium and the oxalic acid radical. Klein obtained similar results when he attempted to prepare a double oxalate of potassium and tellurium (*Ann. Chim. Phys.*, 1887 [6], x., 108; *Bull. Soc. Chim.*, xlv., 714).

Tellurium Succinate.—A solution of succinic acid was heated with finely divided tellurium dioxide for three months. At no time did a portion of the filtered solution respond to a test for tellurium. There is apparently no action between tellurium dioxide and succinic acid.

Tellurium Dioxide and Certain Other Organic Acids.—An excess of tellurium dioxide was also heated with concentrated solutions of malic, gallic, and lactic acids for long periods of time. All of these acids slowly dissolved small amounts of tellurium dioxide. In the case of malic and gallic acids, crystals could be obtained which contained small amounts of tellurium, but it was impossible to separate the tellurium containing substances from the free acid. The solution obtained in lactic acid failed to yield any crystals after concentration by various methods. It was evident that if a definite oompound was formed it was soluble in the liquid lactic acid. In none of these cases was there a separation of elementary tellurium during the long periods of heating, as was the case with tartaric acid.

Klein (*loc. cit.*) had similar experience with tellurium dioxide and phosphoric acid. A reaction between these two compounds could be recognised. He states, however, he was entirely unable to separate out a definite compound containing tellurium and phosphoric acid.

Tellurium Oleate.—Tellurium tetrachloride proved to be easily soluble in anhydrous benzene. Kahlenberg (*Journ. Phys. Chem.*, 1902, vi., 1) has shown that if a solution of copper oleate in benzene is treated with a metallic chloride dissolved in benzene, a brown precipitate of anhydrous copper chloride is produced with the metallic oleate. This suggested a means of preparation of tellurium oleate and certain other compounds of tellurium with the higher fatty acids.

A solution of purified copper oleate in anhydrous benzene was treated with an excess of a solution of tellurium tetrachloride in benzene. A precipitate of brown anhydrous copper chloride immediately formed. The precipitate was gelatinous and extremely difficult to filter. Before filtration could be effected, a purple colour developed in the solution and in the precipitate. This indicated that if tellurium oleate had originally been formed, it rapidly dissociated into colloidal tellurium and free oleic acid.

Various attempts were made to salt out an oleate of tellurium from the solution immediately after precipitation. As "salting out" agents, water, as well as organic liquids in which the metallic oleates are usually insoluble, were used, but the tellurium always separated in the elementary form before a definite compound could be obtained.

Final attempts were made by using molecular proportions of the two reagents dissolved in benzene. The benzene was carefully removed at a temperature not exceeding 65° C. The remaining black residue consisted of a mixture of free oleic acid, copper chloride, and elementary tellurium.

It is therefore evident that these methods do not offer a means of preparation of this compound. Results show that tellurium oleate is probably produced, but tellurium and oleic acid are so weakly basic and acid, respectively, that the compound immediately dissociates into elementary tellurium and free oleic acid.

A number of similar experiments were carried out with copper stearate solutions but with identical results.

Summary.

1. A detailed method for the preparation of tellurium acid tartrate has been given. It was found that this salt cannot be separated from tartaric acid by crystallisation. This is contrary to the findings of Becker.

2. Tellurium acid citrate—$Te(HC_6H_5O_7)_2$, is produced by the action of a concentrated solution of citric acid on tellurium dioxide. This salt crystallises in white, opaque, radiating crystals. It differs from the acid tartrate in that its solutions will withstand boiling temperatures without

reduction and its solubility is sufficiently less than that of the free acid to permit purification by fractional crystallisation.

3. Succinic acid does not attack tellurium dioxide.

4. Oxalic, lactic, malic, and gallic acids hold appreciable amounts of tellurium dioxide in solution. It was impossible to separate a crystalline compound of tellurium with any of these acids.

5. The existence of an oleate or stearate of tellurium has been shown to be doubtful.

The author takes pleasure in acknowledging his obligation to Prof. Victor Lenher, at whose suggestion and under whose guidance and inspiration the work of this and the preceding paper (which will appear later) has been carried out.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

(Continued from p. 161).

THE very marked falling off in the yield of sulphur trioxide with rising temperature is in harmony with the well known physico-chemical principle associated with the name of Le Chatelier, viz., that if any change in the external conditions (pressure and temperature) is imposed on any system in equilibrium, then the equilibrium shifts in such a direction as to meet and partially neutralise the change in question.

If, for example, the temperature of a closed vessel containing only water and water-vapour is raised, some of the water will evaporate until the vapour pressure has risen to the value appropriate to the higher temperature. Evaporation, however, is accompanied by absorption of heat, and the equilibrium between water and water-vapour shifts therefore with rise of temperature in that direction which involves a partial neutralisation of the heat communicated from the outside.

So with any reversible chemical reaction, if the temperature of the equilibrium mixture is raised, the position of equilibrium shifts in that direction which involves absorption of heat. Now, the formation of sulphur trioxide from sulphur dioxide and oxygen is an exothermic process; *i.e.*, the change $2SO_2+O_2=2SO_3$ is accompanied by the evolution of heat, and it therefore follows that the reverse process—the dissociation of the trioxide—involves absorption of heat. Rise of temperature accordingly favours the formation of the system sulphur dioxide + oxygen at the expense of the sulphur trioxide.

The influence of temperature on the equilibrium constant K of a reaction, and its relation to the heat effect of the reaction is expressed in the thermodynamic equation—

$$\frac{d(\log_e K)}{dT} = -\frac{Q}{RT^2},$$

where Q is the quantity of heat liberated when the reaction goes completely from left to right at the absolute temperature T, and R is the well-known gas constant. It appears that the value of Q for the reaction $2SO_3=2SO_2+O_2$ is a linear function of the temperature, and may be represented by the equation $Q=-47{,}300+4T$. If this value of Q is put in the foregoing thermodynamic equation, and the latter is then integrated, a formula is obtained which expresses the variation of K with the temperature, viz.:—

$$\log_{10} K = -\frac{10373}{T} - 2{\cdot}222 \log_{10} T + 14{\cdot}585.$$

The values of K given by this equation are in close agreement with the experimental figures.

The Le Chatelier principle referred to above makes it possible to predict the effect of increasing the pressure on any equilibrium system at constant temperature. If, for example, ice and liquid water are in equilibrium at 0° C., and a bigger pressure is applied, the system meets this by shrinking; *i.e.*, the equilibrium shifts so as to increase the proportion of the denser constituent (liquid water) at the expense of the lighter (ice). Similarly, with any reversible chemical reaction at a given temperature, increase of pressure favours the formation of the system occupying the smaller volume, and the equilibrium accordingly shifts in that sense.

In the equilibrium represented by $2SO_3 \rightleftarrows 2SO_2+O_2$, the number of molecules on the left being two, that on the right three, it is clear that the sulphur trioxide occupies a smaller volume than the sulphur dioxide and oxygen from which it is formed. Hence increase of pressure at any temperature would lead to a greater percentage conversion of the dioxide into the trioxide. If the maximum yield of sulphur trioxide obtainable at the ordinary pressure and at all temperatures within the possible working range were comparatively low, then it might be desirable, even on the manufacturing scale, to carry out the contact process under pressure. Since, however, that contingency does not arise, the question of operating under pressure does not present itself in any practically urgent shape.

The law of mass action, then, coupled with the principles of thermodynamics, leads to a complete quantitative presentation of the equilibrium between sulphur trioxide, sulphur dioxide, and oxygen, as it exists over a fairly wide range of temperature, and if the yield were the only factor to be considered in the contact process, it is plain that the lower the working temperature the better. The manufacturer, however, has to take another factor into account, and that is the time required at each temperature for the establishment of the equilibrium. The velocity of chemical reactions, as shown by innumerable physico-chemical investigations, has a very big temperature coefficient, and as a rule is doubled or trebled for a rise of 10° C. The contact process is no exception to this rule, and the rate at which sulphur dioxide and oxygen combine to form sulphur trioxide in presence of a catalyst increases very rapidly with rising temperature.

The practical question is whether, at those temperatures for which the yield approaches 100 per cent, the reaction proceeds *to equilibrium in a reasonably short time*. Clearly the manufacturer might prefer a somewhat lower yield of the trioxide, combined with a greater rate of reaction, than an almost quantitative yield with a slow reaction and the extra costs which this would involve. Such a question must manifestly be decided in favour of those working conditions which give the best economic return.

Fortunately, in the case of the contact process, it is possible to operate with satisfactory speed even at temperatures as low as 400—500°, where the percentage yield is still very high. This possibility is due to the fact that platinum, in one form or another, is such an efficient catalyst of the reaction between sulphur dioxide and oxygen. Other and less efficient catalysts, such as the ferric oxide obtained by roasting pyrites, can be and are employed, but the establishment of equilibrium at 400—500° in such cases would be a very slow and uneconomical process. When ferric oxide is used as catalyst in the contact process, the balance between yield and rate of change is struck by working at about 600°. Not until this temperature is reached does the reaction in presence of ferric oxide become reasonably rapid. The yield under these conditions goes down to 60—70 per cent, but against this may be put the fact that this is achieved by the use of a cheap contact substance. When ferric oxide is used as the catalyst, as in the Mannheim process, the unchanged sulphur dioxide may, after removal of the trioxide by absorption, be passed into a second converter in which a platinum catalyst is employed.

* Canton Lecture (I.). Delivered before the Royal Society of Arts, December 2, 1918. From the *Proceedings of the Royal Society of Arts*, xvii, No. 3450.

Another important technical gas reaction which is of peculiar interest from the standpoint of these lectures, and has been of great significance in connection with the war, is the synthesis of ammonia from nitrogen and hydrogen. In the case of the sulphuric acid contact process, the technical development was largely independent of and anterior to the application of physico-chemical principles, however valuable these may now be in formulating the influence of varying conditions and in giving quantitative expression to the possibilities of the process. In the synthesis of ammonia, on the other hand, the physico-chemical investigation came first, and the large-scale process now operated is the direct outcome and development of work carried out on purely scientific lines.

It has long been known that when electric sparks are passed through ammonia gas for some time it splits up into the constituent elements, but Deville pointed out about fifty years ago that even after prolonged sparking there was still a trace of ammonia left, as was proved by the faint white cloud formed when a little hydrogen chloride gas was mixed with the decomposition products. Deville further succeeded in showing that a minute quantity of ammonia is produced when a mixture of nitrogen and hydrogen is passed through a heated tube.

The real recognition of the decomposition of ammonia as a reversible reaction came, however, much later, and the application of the principles of chemical equilibrium to this case belongs to quite a recent period. In 1905 Haber showed that if ammonia is passed over finely-divided iron at a high temperature (about 1000° C.) a small quantity of the gas escapes decomposition; and, further, if the residual nitrogen and hydrogen, now freed from ammonia, is passed over finely-divided iron at the same temperature as before, fresh ammonia is generated, the quantity being practically equal to that which escaped decomposition in the first instance. It is clear, therefore, that the reaction is a reversible one, and may accordingly be written $N_2+3H_2 \rightleftarrows 2NH_3$, although there is no doubt that at 1000° C. and the ordinary pressure the equilibrium position lies almost at the system represented by the left-hand side of this equation.

It is instructive and, as it turns out, of the highest practical significance, to study the influence of changing pressure and temperature on the ammonia equilibrium. In this investigation Le Chatelier's principle is again a trustworthy guide. It has already been stated that in any reversible chemical reaction which has reached equilibrium an increase of pressure at constant temperature favours the formation of the system occupying the smaller volume, and shifts the equilibrium in that sense. The application of this theorem to the ammonia equilibrium $N_2+3H_2 \rightleftarrows 2NH_3$, leads to the conclusion that the equilibrium mixture at any temperature will contain a greater proportion of ammonia when the pressure is high than when it is low. If the object is to produce ammonia by the union of hydrogen and nitrogen, then the yield will be increased by working under high pressures.

A more definite formulation of this pressure effect is possible when we turn to the equilibrium constant and express it, not in terms of the equilibrium concentrations of nitrogen, hydrogen, and ammonia, but in terms of their equilibrium partial pressures, p_{N_2}, p_{H_2}, and p_{NH_3}. On this basis

$$\frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}} = \text{const. at a given temperature, or alternatively,}$$

$$K = \frac{p_{NH_3}}{p^{\frac{1}{2}}_{N_2} \cdot p^{\frac{3}{2}}_{H_2}}.$$

Now, at high temperatures p_{NH_3} is known to be small compared with p_{N_2} or p_{H_2}, and so long as this condition holds no great error is involved in writing $p_{N_2}+p_{H_2}=P$, where P is the total pressure of the three gases. Further, where the nitrogen and hydrogen have been taken in the volume proportion 1 : 3, $p_{H_2}=3p_{N_2}$. When these relationships are coupled with the equation for the equilibrium constant it follows that $p_{NH_3}=0{\cdot}325K \times P^2$—that is, the partial pressure of the ammonia in the equilibrium mixture is, for low concentrations of ammonia, proportional to the *square* of the total pressure.

The percentage of ammonia by volume (x) in the equilibrium mixture will be given by—

$$x = \frac{p_{NH_3}}{P} \times 100 = 0{\cdot}325 \text{ K} \times \text{P},$$

and it is therefore to be expected that x will increase approximately in proportion to the total pressure of the reaction mixture. This prediction is confirmed by experiments in which Haber showed, for example, that the volume percentage of ammonia in the equilibrium mixture at 800° and a pressure of one atmosphere was about 0·012, whereas under a pressure of thirty atmospheres at the same temperature the percentage was 0·34; *i.e.*, nearly thirty times as great.

The approximate proportionality between the volume percentage of ammonia in the equilibrium mixture and the total pressure is further emphasised by the figures given below (Haber), which show the exactly calculated influence of high pressures on the position of equilibrium at different temperatures. It will be observed, on reference to these figures, that the proportionality between the percentage of ammonia and the pressure is most exact where the values of the former are low. Where these values become appreciable their increase is somewhat less than proportional to the rise of pressure.

At an early stage in the experimental investigation it was recognised that a rise of temperature was inimical to the conversion of nitrogen and hydrogen into ammonia, but this is only what could be foreseen on the basis of Le Chatelier's theorem. For the combination of nitrogen and hydrogen to form ammonia is accompanied by the evolution of heat, and since rise of temperature invariably shifts an equilibrium in the direction which involves absorption of heat, it follows that the percentage of ammonia obtainable from the two gases diminishes as the temperature rises.

This may be put more definitely with the help of the thermodynamic equation—

$$\frac{d \log_e K)}{dT} = -\frac{Q}{RT^2},$$

already quoted in connection with the sulphur trioxide equilibrium. If the relation between specific heat and temperature is known for each of the gases concerned in a gaseous reaction, the variation of the heat effect Q can be formulated, for, according to Kirchhoff's theorem, $\frac{dQ}{dt} = C_1 - {}_2$, where C_1 is the sum of the molecular specific heats of the reacting substances at constant pressure, and C_2 is the corresponding quantity for the resulting products. In the case of the ammonia reaction C_1 is the true specific heat at constant pressure of a mixture of $\frac{1}{2}$ grm. molecule of nitrogen+$\frac{3}{2}$ grm. molecule of hydrogen, and has been found to be $13{\cdot}47+0{\cdot}00164\ t$, where t is temperature centigrade. The quantity C_2, on the other hand, is the true specific heat at constant pressure for 1 grm. molecule of ammonia, and is given by the equation $C_2=8{\cdot}62+0{\cdot}0035\ t+5{\cdot}1 \times 10^{-6}\ t^2$. If these expressions are inserted in the Kirchhoff formula $\frac{dQ}{dt} = C_1 - C_2$, and this is integrated, then—

$$Q=Q_0+4{\cdot}85t-0{\cdot}00093t^2-1{\cdot}7 \times 10^{-6}t^3 \text{ grm. calories.}$$

The constant Q_0 represents the heat evolved in the reaction $\frac{1}{2}(N_2+3H_2)=NH_3$ at 0° C., and has been found to be 10950 cal., so that the heat effect of the foregoing reaction at t° C. is given by—

$$Q=10950+4{\cdot}85t-0{\cdot}00093t^2-1{\cdot}7 \times 10^{-6}t^3.$$

If this expression for the heat of reaction is put in the equation—

$$\frac{d(\log_e K)}{dT} = -\frac{Q}{RT^2},$$

and the latter is then integrated, a formula is finaily obtained which represents the equilibrium constant of the ammonia reaction as a function of temperature. The formula so foand by Haber is—

$$\log_{10} K = \frac{2098}{T} - 2\cdot5088 \log_{10} T - 0\cdot0001006\ T + 0\cdot186 \times 10^{-6}\ T^2 + 2\cdot1.$$

The valuee of K calculated in this way are in remarkably good agreement with the experimental determinations of the ammonia equilibrium, as is shown, for example, by the measurements made at thirty atmospheres pressures and various temperatures : —

t° C.	K × 10⁴ found.	K × 10⁴ calc.
561°	21·3	21·5
620°	12 6	12 7
700°	6 80	6 88
722°	5·82	5·92
801°	3·56	3 00
901°	2 13	2·11
952°	1·68	1·66

To be continued).

THE

PRODUCTION OF NITROGEN COMPOUNDS.*

By JACK P. MONTGOMERY, Department Chemistry and Chemical Engineering, University of Alabama.

(Concluded from p. 164).

Production now Normal.

It is estimated that the production of nitrogen compounds by the two ammonia fixation precesses and from the distillation of coal have now reached the annual rate, calculated on the comparative basis of nitrogen and not differentiating the various compounds, for the synthetic processes 100,000 tons, coal distillation 300,000 tons, and cyanamide process 325,000 tons. This is about equal to the total annual amount of nitrogen used in the world prior to 1914.

Nitric acid is now made by three methods, from sodium nitrate by distillation with sulphuric acid, by the oxidation of ammonia, and by the direct oxidation of atmospheric nitrogen. The strongest nitric acid of commerce is made by distilling sodium nitrate with sulphuric acid. In fact this is the only convenient or workable method for making the concentrated acid suitable for nitrating. The other methods of making nitric acid give a weak product which must be concentrated. It is far cheaper to import the sodium nitrate from Chile and make the concentrated acid directly from it than to concentrate the dilute acid made by the other two processes. Until a very few years ago, certainly prior to the beginning of the present century, the nitrate beds of Chile were more important that all the other sources of nitrogen combined, and that source is still of greater importance than any other one source of nitrogen compounds. In 1914, before the beginning of the war, the production of Chilean nitrate, including that used by Germany, was at the annual rate of 3,000,000 tons, and in 1918, with none going to Germany, the production was 3,700,000. This sodium nitrate wss used to a great extent directly as a fertiliser. It was also used, and particularly during the war, as a source of nitric acid for use in the manufacture of munitions. Although vast quantities of nitrates may be made from atmospheric nitrogen and from the oxidation of ammonia, sodium nitrate may be expected to maintain its importance for many years. It will be used primarily as the source of the concentrated nitric acid and will not lose its importance as a fertiliser. The U. S. Department of Agriculture last winter, in spite of the fact that the war was being prosecuted, made arrangements to sell to the farmers of the country a great volume of Chilean nitrate, and during the present winter even more is to be imported for this purpose. This is an index of the importance of sodium nitrate as a fertiliser and evidence that it is not in danger of being forced into obscurity.

Direct Oxidation of Nitrogen.

The direct oxidation of the nitrogen of the air in the manufacture of nitric acid constitutes the remaining method for the fixation of atmospheric nitrogen to be described. As long ago as 1785 Cavendish noted that oxides of nitrogen could be obtained by passing an electric spark through air in an inclosed space. It is a matter of record that he made dilute nitric acid by tbis process. In 1901 Bradley and Lovejoy established at Niagara Falls a factory using this method of making nitric acid from atmospheric nitrogen. Their apparatus consisted of two concentric cylinders carrying platinum electrodes regularly spaced on the inside surface of the outer cylinder and on the outside surface of the inner cylinder. The apparatus was so arranged that as the inner cylinder revolved arcs were sprung between adjacent electrodes on the two cylinders, and as the electrodes moved apart the arcs were strung out until they were extinguished. Air was passed through the space in which the arcs wete formed and some nitric oxide was produced. This was oxidised further to nitrogen peroxide, which was absorbed in towers, forming nitric acid, with water. This apparatus did not prove a commercial success, but paved the way for other attempts.

Birkeland and Eyde met with better success in Norway and their work was improved upon by Schönherr and by Paulding. In each of these processes there are devices to cause the production of large arcs with large surfaces through which the air is forced at a regular rate. The first reaction is represented by the equation—

$$N_2 + O_2 \rightleftarrows 2NO.$$

It was formerly thought that the nitric oxide was produced by a thermal effect, but it has been recently shown that the forward action in the above equilibrium is induced by the electrical effect, while the backward action, involving the decomposition of the nitric oxide, is thermal. A study of the equilibrium conditions in the above system revealed the fact that if the gases were not cooled with great rapidity the backward action is fast enough to undo the work of the arc to such an extent that the process could not be a success. This, in fact, was the key to the solution of the whole problem, and the achievements of Birkeland and Eyde and their associates were due in large measure to the p ovisions made for rapidly cooling the mixture issuing from the furnaces in which the air had passing through the arcs. This cooling is accomplished by passes the gases through the tubes of specially designed boilers in which the excess heat was used in the production of steam. The mixed gases issuing from the boiler tubes are at about 150° C. and at that temperature the decomposition of the nitric oxide is negligible. Under these conditions of rapid cooling the nitric oxide content of the gases coming from the arc furnaces may be worked up to 1·5 per cent.

On further cooling the nitric oxide takes up oxygen from the air according to the equation—

$$2NO + O_2 \rightarrow 2NO_2$$

By interaction with water nitric acid is formed as follows :—

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

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* *Chemical Engineer*, xxvii., No. 2.

This interaction occurs in absorption towers and the product is dilute nitric acid, which may be neutralised with lime to form calcium nitrate, which in turn is used as a fertiliser or as a source of concentrated nitric acid.

Cheap Power not Necessary.

It is popularly believed that the arc process for the direct production of nitric acid from atmospheric nitrogen can be profitably carried out only where there is cheap and abundant water power, as is the case in Norway, but, as was pointed out above, the success of the process depends rather upon attention paid to the equilibrium conditions. This process is admirably adapted for use whereever there is a source of current with an off peak load for some hours each day. It takes very little time to get the process under way, and it has been suggested that small units should be established at a number of hydro-electric power plants where for a part of the day the power is not being developed or used. Another interesting development or extension of this process may be expected in connection with by-product coke plants which have a large volume of gas going to waste. The gas will be used to operate gas engines, the power from which will be employed for the generation of the required current for a small number of arc furnaces producing nitric acid from atmospheric nitrogen. The nitric acid produced will be neutralised by the ammonia from the by-product plant and the product will be ammonium nitrate. Thus the by-product plant will not only save the cost of the sulphuric acid now employed for the absorption of the ammonia, but will be making a valuable product instead.

The present production of nitric acid by the various arc processes is about 65,000 tons per year. If the suggestions made concerning the installation of small units at various power plants and at by-product plants are well received by those in charge of such enterprises we may expect to see within the next few years a great increase in production of nitrates by the arc processes.

Synthetic Ammonia Process.

A very recent method for the preparation of nitric acid has been referred to in the case of the cyanamide and the synthetic processes for making ammonia. In the operation of each of these processes some of the ammonia is oxidised to nitric acid, which is then combined with the balance of the ammonia resulting in the formation of ammonium nitrate. This method is a development of the Ostwald process for the oxidation of ammonia. In this process a mixture of ammonia and air in the proportion by volume of one of the former to ten of the latter is passed at a high speed through a platinum gauze heated to about 700° C. The gauze is made of wire 3/1000 of an inch in diameter and there are eighty meshes to the inch. The gas is passed at such a rate that the contact time is about 1/100 of a second. The platinum gauze is first heated by the passage of a current, but as the reaction is exothermic it is not necessary to maintain the heat during the oxidation.

If the ammonia and air mixture are passed through too rapidly the gauze is cooled below the reacting temperature and the ammonia passes through unchanged. If, on the other hand, the stream of gas is too slow, the oxidation may result in the entire loss of nitrogen by the formation of water and elementary nitrogen. The reaction aimed at is—

$$4NH_3+5O_2 = 4NO+6H_2O.$$

A great deal of work has been done to determine the best temperature, size of the catalyst, speed of the gases, and conditions of cooling to obtain the highest efficiency. This process is now so well controlled that an efficiency of well over 90 per cent is the usual practice.

What was said in regard to the necessity of rapidly cooling the nitric oxide obtained in the arc process applies here with equal effect, and the nitric oxide obtained by the oxidation of ammonia is cooled as rapidly as possible and further oxidised to nitrogen peroxide by the oxygen of the air. The further details of making nitric acid by this process are the same as those already mentioned in the case of the arc process.

An interesting application of the process for the oxidation of ammonia to nitric oxide is employed in some modern sulphuric acid plants which produce sulphuric acid by the chamber process. Instead of employing sodium nitrate as the source of the oxides of nitrogen required for the catalyst in this process, a small installation of a modified Ostwald apparatus is installed and ammonia is oxidised as needed. This utilisation of ammonia is said to materially reduce the production cost of the sulphuric acid.

To summarise, the important compounds of nitrogen are ammonia and ammonium salts, nitric acid and the oxides of nitrogen, and the organic nitrogenous materials produced in agriculture. The sources of these compounds are Chilean sodium nitrate, bituminous coal, and atmospheric nitrogen. The processes of importance for the production of ammonia are the "natural" one of obtaining it as a by-product in the distillation of coal and other bituminous materials, the synthetic process for utilising atmospheric nitrogen, and the cyanamide process for making ammonia indirectly from the nitrogen of the air. The processes for making the oxides of nitrogen are the arc process for the fixation of atmospheric nitrogen and the oxidation of ammonia. Nitric acid is made by the interaction of nitrogen peroxide with water, the oxide of nitrogen being obtained by one of the processes just mentioned, and by the distillation of a mixture of sulphuric acid and sodium nitrate. Nitrogenous materials are produced in agriculture when nitrogenous fertilisers are employed in the cultivation of crops and in those cases where by symbiosis the atmospheric nitrogen is directly employed.

As to whether or not man by his efforts has prevented the nitrogen equilibrium from being upset in the wrong direction there is now no question. Even with a destructive war in progress enough nitrogenous material was being manufactured or rendered available to maintain the rate of loss for some time to come. Now that military demands have so nearly ceased, the supply of nitrogen compounds is far greater than the apparent immediate need. Have we gone too far in constructing plants for the production of nitrogen compounds? This is a question which only the future can answer. It is certainly a present fact that the production of nitrogen compounds is far greater than any peace demand which we could have imagined, and yet there are millions of acres of land which would richly respond to more intensive cultivation for which our stores of nitrogenous materials should be used. There must be a period of patient waiting and re-adjustment, and during this time we may be tempted to think that we have gone too far in the production of nitrogenous materials. But many thoughtful observers predict that finally there will be a demand for all our present production of nitrogen compounds, and more.

Man sought to maintain the nitrogen balance and to prevent loss in the supplies of a valuable material. Not only has he accomplished this but he has added greatly to the store. This feat, stimulated by the world war, may in time result in making conditions of living so sure upon the earth that we may forget the great destructions that would have been impossible but for nitrogen compounds, and remember rather the constructive effects of these same compounds in rebuilding the world.

Silvanus Thompson Memorial Lecture. — The Council of the Röntgen Society have pleasure in announcing that the second lecture, entitled "The Electrical Changes in Active Tissues," will be delivered by Prof. W. M. Bayliss, M.A., D.Sc., F.R.S., on Tuesday, May 9, 1919, at 8 p.m., in the Barnes Hall, at the Royal Society of Medicine, 1, Wimpole Street, London, W. 1.

NOTE ON THE EXTRACTION OF THALLIUM FROM PYRITES FLUE DUST.

By GEORGE SISSON and J. S. EDMONDSON.

During the progress of the war the Research Department of the Ministry of Munitions requested chemical manufacturers to investigate their waste products, with a view to recovering useful substances. They mentioned more particularly selenium from sulphuric acid works, this element being valuable on account of its property of altering its electrical conductivity when subjected to light of varying colour or intensity. In response to the above request, we collected for experiment a quantity of dust and refuse deposited in the flues of the sulphuric acid plant of the Blaydon Chemical Works. The flues mentioned lead the sulphur gases from the pyrites kilns into the Glover concentrating tower, and require to be cleared out periodically. The kilns are charged with copper pyrites from Spain. Such pyrites contain perhaps 2 per cent of copper and small quantities of a large number of other elements. Some of the constituents, such as arsenic, antimony, tellurium, thallium, selenium, are volatilised or burnt off with the sulphur, the iron, copper, &c., remaining in the burnt ore. The more volatile constituents, such as the sulphur, arsenic, and selenium, are carried forward principally beyond the flue into the Glover tower.

The flue dust itself consists of materials carried over mechanically such as iron oxide, small quantities of copper and lead, and volatile substances condensed at the flue temperature of about 450° C., such as antimony, bismuth, thallium, &c.

After making several experiments on this material we failed to separate any appreciable quantity of selenium; no doubt the temperature of that part of the plant was too high for condensation, the hot gases carrying forward into the sulphuric acid any traces of selenium contained in the pyrites.

We then turned our attention to thallium, which was known to occur in such deposits. In fact the metal was descovered in and isolated by Crookes from a similar deposit from the Harz Mountains ore (Chemical News, 1861, iii., 193, 303). Lamy also isolated a specimen from a lead-chamber deposit in 1862 (*Ann. de Chim.* [3], lxvii., 385).

Although thallium compounds are somewhat widely distributed they occur in very small quantities, associated with other metallic sulphides in various ores, and the flue dust of sulphuric acid factories is still the only practicable source. Such dust may contain up to 8 per cent, but only rarely is more than 0·25 per cent of thallium present. The quantity of dust we collected was about 15 cwt. in six months, representing the burning of 1500 tons of pyrites. The dust contained 0·25 per cent or a total of 4 lb. of thallium, equal to 1 part per million of pyrites.

The method we used to separate the thallium depends chiefly upon the sparing solubility of the chloride and the solubility of the sulphate, the operation being to treat the dust with boiling water acidified with sulphuric acid in a wooden or earthenware vessel, using live steam injection; on settling, the clear liquid is treated with hydrochloric acid. The crude chloride precipitate is separated, washed, and converted into sulphate by heating with strong sulphuric acid, the excess of acid is driven off, the remaining sulphate dissolved in water, filtered, and re-precipitated as chloride. The purified chloride after drying is mixed with potassium cyanide and sodium carbonate, and fused in a crucible, care being taken not to use too high a temperature in order to avoid loss by volatilisation. Or the chloride may be reduced by zinc and the resulting metal melted in a current of inert gas. Instead of hydrochloric acid sodium chloride may be used to precipitate the thallium from the sulphate solution. The crude dust must be washed repeatedly to extract the whole of the thallium salt. Several ounces of the metal were obtained by this method.

An alternative method is to precipitate the thallium as iodide from the sulphate solution, the iodide being less soluble than the chloride, but the cost of the iodide is an objection.

Discussion.

Prof. P. Phillips Bedson suggested that it might be possible to take advantage of the change of colour which occurred on heating thallium iodide in determining the heat of bearings, as had been done in the case of mercuric iodide. He recalled that in 1901 he had assisted in a search for thallium among alkali waste materials, but without success.

Mr. Edmondson, in reply to a question, said that thallium was not found in all samples of pyrites.—*Journal of the Society of Chemical Industry*, xxxviii., No. 6.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 27, 1919.

Sir J. J. Thomson, O.M., President, in the Chair.

The following papers were read :—

"*The Morphology and Evolution of the Ambulacrum in the Echinoidea.*" By H. L. Hawkins.

A summarised account of the ambulacra in non-Hoelectypoid orders is given. *Bothriocidaris* shows the simplest type of structure, and the most efficient for coronal strength. As podia increased, ambulacral plates multiplied, and the areas became mechanically weak. The main podial function in Regular Echinoids being adhesive, coronal weakness demanded modification. In most Palæozoic types, general flexibility neutralised local weakness; but with the adoption of rigidity the problem reappeared. Hence arose "plate-complexity."

The formation of compound plates is discussed. "Grouping" precedes, and is distinct from, combination. Plate-reduction is due to "growth-pressure"; combination to tubercle-growth. Elaboration of combination culminates in the Echinometridæ, where the compounds regain "Bothriocidaroid" proportions.

In Irregular Echinoids no combination occurs; grouping is often developed. Secondary specialisation in Spatangids produces "Palæozoic" structures.

The Holectypoida show four ambulacral types :—

(i.) Plesiechinid (triad-groups adorally, primaries adapically);
(ii.) Pygasterid (primaries throughout);
(iii.) Pyrinid (triad-groups throughout);
(iv.) Discoidiid (triad-groups adorally, dyad-groups adapically).

Plesiechinid is primitive, and resembles the early Acrosaleniid type. Pygasterid indicates simplification, being morphogenetically transitional from Diademoid to Spatangid structure. Pyrinid is persistent, resembling the "Echinoid" structure of Diademoids. Discoidiid is exceedingly elaborate, showing extreme plate-reduction.

The Cassiduloidea are divided into Nucleolitoida and Cassiduloida (restr.). The former is related to the Pygasteridæ; its simpler members have Plesiechinid ambulacra, and Holectypoid structures appear in later forms. The Cassiduloida evolved through the Echinoneïdæ.

There are three main trends of evolution in Echinoid ambulacra :—(i.) Diademoid, attaining plate-combination; (ii.) Clypeastroid, attaining plate-destruction; and (iii.) Spatangoid, reversionary.

"*The Genesis of Œdema in Beriberi.*" By R. McCarrison, M.D.

CHEMICAL SOCIETY.

Ordinary Meeting, March 6, 1919.

Sir William J. Pope, K.B.E., F.R.S., President, in the Chair.

The President announced that Prof. Dr. T. Schlœsing, who was elected an Honorary and Foreign Member on June 16, 1892, died on February 8 last, and that Mr. Harry Shulman, who was elected a Fellow on February 18, 1915, had died on February 22.

Messrs. G. J. Woods, F. C. Savage, N. Makower, R. Bickmore, G. Higson, W. A. Nash, B. R. Heasman, C. Diamond, F. Peet, and W. C Peck were formally admitted as Fellows of the Chemical Society.

The names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council for 1919-1920 were read from the Chair.

Certificates were read for the first time in favour of William Herbert Fletcher Armstrong, B.A., Khalsa College, Amritsa, India; Walter Hatton Crouch, 67, Wellington Road, Wanstead, Essex; James Ross Fraser, 13, Archibald Road, Tufnell Park, N. 7; James Edward Grainger, Lennards, Rainham, Essex; John Henry Harvey, Ravensworth, Llantarnam, Newport, Mon.; George Armand Robert Kon, B.A., 79, Cromwell Road, S.W. 7; Walter Shepherd, 103, Spotland Road, Rochdale; Walter Bernard Smith, B.Sc., Marlborough College, Wilts; Ernest Henry Stenning, King William's College, Isle of Man; Frederick Thomas Stevenson, 48, Strathnairn Street, Bermondsey, S.E.; Ralph William Ewart Stickings, B.Sc., Soudley House, Wandle Road, Morden, Mitcham; Stanley Goulden Thompson, 1, Thorn Bank, Manchester Road, Buxton, Derbyshire; Harold George Tribley, Yetminster, Sherborne, Dorset; Albert Edward Wallis, "Hillside," Sunbridge, Sevenoaks, Kent.

A certificate for election has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of David M. Davies, H.M.S. *Cyclops*, care of G.P.O.

Prof. J. W. Nicholson, M.A., D.Sc., F.R.S., then delivered his lecture, entitled "Emission Spectra and Atomic Structure."

A vote of thanks to Prof. Nicholson for his lecture, proposed by Prof. W. H. Bragg, F.R.S., and seconded by Sir James Dobbie, F.R.S., was carried with acclamation.

Ordinary Meeting, March 20, 1919.

Sir William J. Pope, K.B.E., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of William Henry Barrett, Rossall School, Fleetwood; Robert Macfarlane Clark, B.Sc., 138, Bath Street, Glasgow; Harry Eade Dear, B.Sc., Littlecote, Widemouth Bay, Bude, Cornwall; Surindra Nath Dey, B.A., 38/1, Nilmony Mitter Street, Beadon Square, P.O., Calcutta, India; Reginald Gordon Doyle, 28, Newlands Park, Sydenham, S.E. 26; Frederick Freeth, 17, Victoria Road, Stockton Heath, Cheshire; Frederick John Spencer Hall, 4, York Road, Forest Gate, E. 7; Edward John Jones, 8, Windsor Street, Uplands, Swansea; Frederick George Mann, B.Sc., 21, Thurlby Road, W. Norwood, S.E. 27; George Stanley Withers Marlow, B.Sc., 37, Collington Road, Sydenham, S.E. 26; Frank Matthews, B.Sc., 12, Hurlingham Court Mansions, S.W. 6; James Morris, 23, Brynymor Crescent, Swansea; Marriappa Parthasarathy, 21, Maligakande, Colombo, Ceylon; John David McBeath Ross, M.A., B.Sc., 9, Ruskin Walk, Herne Hill, S.E. 24; Kalyan Chennakesava Srinivasan, M.A., Niton, 34, Pycroft's Road, Madras, S.E., S. India; Cyril Heath Stephenson, B.A., Darley Green, Knowle, Warwickshire; Ernest Turner, B.Sc., 28, Shrewsbury Terrace, South Shields; Walter Wahl, Academy, Abo, Finland; Ott Walker, 29, Camden Street, Belfast.

The following papers were read :—

"The Rotatory Dispersive Power of Organic Compounds. Part IX. Simple Rotatory Dispersion in the Terpene Series." By T. M. Lowry and H. H. Abram.

"The Formation and Stability of *spiro*-Compounds. Part II. Bridged-*spiro* compounds Derived from *cyclo*-hexane." By C. K. Ingold and J. F. Thorpe.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 2, 1919.

Dr. Samuel Rideal, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Charles Frederick Lee Barber, A.I.C.; George Stanley Withers Marlow, B.Sc., F.I.C.; Frederick William Read.

Certificates were read for the second time in favour of Messrs. Madanlal Jekisandas Gajjar; James Sorley, F.I.C.

The following were elected members of the Society :— Messrs. Robert Odell Bishop, A.I.C.; Hubert William Bywaters, D.Sc., F.I.C., Ph.D.; Barnard Scott Evans, M C., B.Sc.Lond., F.I.C.; Frank Scott Fowweather, M.Sc., A.I.C.; Robert Atkinson Oddy; William Branch Pollard; Charles Kenneth Tinkler, D.Sc., F.I.C.

The following papers were read :—

"*A Method for the Determination of Monochlorbenzene in Mixtures containing Benzene, Monochlorbenzene, and Dichlorbenzene.*" By N. G. S. Coppin, M.Sc., A.I.C., and F. Holt, O.B.E., M.Sc., A.I.C.

The method is based upon Mr. D. Northall-Laurie's "Determination of Toluene in Commercial Toluols" (*Analyst*, 1915, xl., 384). 200 cc. of the *dried* sample are distilled at the rate of 7 cc. per minute; the first 50 cc. are collected, and after collecting a further 100 cc. exactly, the distillation is stopped. The first 50 cc. and the 50 cc. residue are each tested in special constant boiling-point flasks. From the boiling-points the percentages by weight of the constituents are read off from a graph.

The method gives direct results with an accuracy of 0·1 per cent for all mixtures containing from 50 to 100 per cent of monochlorbenzene.

"*The Electrical Conductivity of Milk.*" By J. H. Coste, F.I.C., and E. T. Shelbourne, F.I.C.

The examination of over 200 samples of milk shows that the conductivity is not sufficiently well defined to be useful as an analytical datum except for milks which have been examined by this means before incurring the risk of dilution. The relation between conductivity and temperature, non-fatty solids, ash, chlorion content, and free acid, and the effect of dilution, have been examined. It is pointed out that the results obtained are consistent with the explanation given by L. C. Jackson and A. C. H. Rothera that the conductivity is dependent on the extent to which the constant osmotic pressure of milk is due to electrolysis with which the milk-sugar is complementary.

"*Note on Soluble Lead in the Glaze of Casseroles.*" By Helen Masters, B.Sc.

Casseroles of various descriptions, particularly some said to be of French make, were found to yield considerable proportions of lead on treatment with 4 per cent acetic acid, and with dilute solutions of other acids such as would be present in certain cooking operations. The soluble lead is not all extracted by one operation, but after two or three treatments each subsequent treatment appears to yield a fairly constant quantity.

SOCIETY OF GLASS TECHNOLOGY.

The March meeting of the above Society was held in the University (Mason College), Birmingham, on Wednesday, March 18.

After the usual formal business, the following paper was read :—

"*The Preparation of Raw Materials for, and the Casting of, Glass Pots.*" By B. J. Allen.

The author dealt first of all with the deflocculation of clays, and showed how it could be accomplished by electrical treatment. He described a simple apparatus for testing clays to show their suitability under this electrical treatment. His experiments have proved that many common fire-clays altogether unsuited in their ordinary state for the manufacture of refractories could by the above treatment be made to produce a large proportion of highly satisfactory material fit to meet the specification for high grade work.

Mr. Allen dealt briefly with the manufacture of pots by the old method of building by hand, and dwelt briefly on the limitations of this method. It is most difficult for the pot maker to guarantee a perfectly united homogeneous pot. It is very essential that clay and the grog be in intimate contact in the finished pot, and this is ensured by the casting of the pot. He then went on to describe in detail the preparation of slip and subsequent casting of pots. He also described in detail different types of pots. The lecture was well illustrated by lantern slides and specimens, and the lecturer gave it as his opinion that research on all these matters should be carried out by the Society.

During the morning, members, at the kind invitation of the Directors in each case, had the opportunity of visiting Messrs. Icknield Glass Works (Oslers), Ltd., Freeth Street, Birmingham, and Messrs. P. Branscomb, Glass (Bottle) Works, Adderley Street, Birmingham.

The members are reminded that the annual general meeting will take place at the University on April 16.

OBITUARY.

Sir JAMES MACKENZIE DAVIDSON.

We regret to have to announce the death of Sir James Mackenzie Davidson, M.B., C.M., which took place at his residence, 26, Park Crescent, Portland Place, on April 2nd.

Sir James was for many years Consulting Surgeon to the Röntgen Ray Department of the Charing Cross Hospital. He took a very prominent part in the early development of the medical application of X-rays, and was among the first to recognise their value in Surgery, becoming one of the most enthusiastic workers in the science. His method of localisation laid the foundation of all subsequent development in this most important branch of X-ray work, and his apparatus is indispensable in practical radiography.

Sir James's researches upon X-rays, radium, and allied phenomena are very extensive; among the more important are—Stereoscopic Radiography and Fluoroscopy, Precise Methods of Localisation of Foreign Bodies in the Eye, contributions to the Physics of the X-Ray, and a Mercury Interrupter for Induction Coils.

His laboratory was always full of interesting work, and he spared no pains or expense in developing his many inventions, working with his own hands.

His well-merited Knighthood was conferred upon him in recognition of his work in the application of X-rays to Medical Science. His striking personality and genial manner will cause him to be greatly missed in his large circle of collaborators.

NOTES.

At *the meeting held at the College of Technology*, Manchester, on January 17, 1919, a paper was read by Mr. Joseph Barnes, on "The Properties and Uses of Some Titanium Compounds," chiefly with regard to its interest to dyers and colorists. The value of titanium compounds in the dyeing industry was recognised by the author forty years ago, who found that this element as well as zirconium gave colour reactions very like alumina. At that time titanium was looked upon as one of the rare elements, but its abundance and wide distribution has since been recognised, and it has been classed by F. W. Clarke as twice as plentiful as carbon. Large quantities of titanium salts are used by leather dressers. The more important salts used are titanium sodium sulphate, titanium potassium oxalate, titanium-tanno-oxalate. The specimens dyed by the aid of titanium that were exhibited by the author were greatly admired.

Investigations carried out by W. E. Tottingham at the Wisconsin Agricultural Experiment Station, Madison, U.S.A., show that during the changes in a fermenting mixture of cow and horse manure an increase in nitrogen was apparent after three and four weeks, the increase being much greater in straw-littered than in unlittered manure. The results showed that the manure contained nitrogen-fixing bacteria of considerable activity, especially when mixed with straw. The chief agent in nitrogen fixation is said to be *Bacterium azophile*, n. sp.

One thing that the war has brought very much into prominence is the preparation of "substitutes." Germany in particular has specialised in this direction. A substitute for milk appears to have been the following :—250 grms. of ground sweet almonds to a litre of water. From the physical, chemical, and alimentary point of view, it approaches very nearly cow's milk. No difference can be perceived when used with tea or coffee. The most suitable after sweet almonds are Brazilian nuts. The following fruits can also be employed, but are not so suitable :—Soya beans, earth nuts, walnuts, cocoanuts, hazel-nuts, and acajou nuts.

Prof. Andrew Grey's new treatise on Gyrostatics and Rotational Motion is an extremely interesting and valuable publication that we hope to review later. The gyroscope has played an important part in military and naval devices during the war and is likely to be applied to many purposes in the future. The very full practical and theoretical treatment of the subject by Prof. Grey, whose work is well known, is likely to be of great use.

M. Cesari (Vétérinarie-major) has made some experiments upon the substitution of albumen from horse blood for white of egg in cooking. Omelettes, rice cake, waffles, &c., in which serum replaced white of egg, were pronounced very good. It was pointed out that 10 litres of serum, at a cost of about 1s. 6d., would replace the whites of 200 eggs worth at least 24s.

The spring meeting of the American Chemical Society will be held in Buffalo early in April. A full and interesting programme has been arranged, in which both social and official functions appear to be well proportioned. The secretary makes a strong appeal for the enrolment of new members, suggesting that "a chemist who is not a member of the American Chemical Society must feel lonesome."

The struggle between M. Pasteur and the medical profession in the early days of his career, is well known, and "The Life of Pasteur," by René Vallery-Radot, and other works, give full accounts of that wonderful fight. But it is interesting to read that the story has been dramatised at the Vaudeville Theatre, Paris, in a five-act play, and is said to have had a very favourable reception, which is all the more remarkable owing to the curious nature of the piece without a plot or a female character, the "human interest" being the struggle and victory of the scientist.

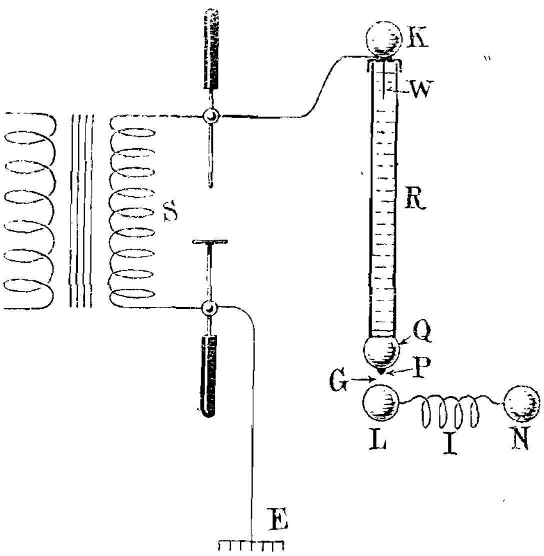
nated consumption of soda-ash in Canada is tons. During the past four years the lack of is been felt by a great many of our industries. entirely dependent on foreign supplies. Most -ash used in Canada came from England, and, war, Canada was practically shut off from Now, however, the Brunner, Mond, Canada, ave their new plant at Amherstburg, Ont., prac- ipleted, and they are in a position to supply requirements. They are using the "Solvay y which practically all the soda-ash now pro- nade. The town of Amherstburg is well nd the raw products—salt, limestone, and are easily available. A tract of land of 650 ecured, and a main building, 170 by 190 feet ries high, was erected. The plant has one of lime kilns known, being 80 feet high. Taken it is one of the most complete soda-ash plants ld, and is designed in such a way that the ty be readily increased with the demand. The oduces its own power, and obtains its salt from cally at the plant. The limestone used is also quarries on the property. The produced soda- neral use in the manufacture of glass, soap, id-pulp, paints, leather, enamelled ware, extiles, oil refining, metal working, and metal- erations, washing powders, chemicals, and

rch issue of *The Industrial League Journal* welve page supplement of an address by The . N. Barnes, M.P., to managers and foremen rial Matters." Mr. H. Blain, of the London ıd Railways, contributes a very interesting Industrial Honour." There are special con- om Mr. Woodman Burbidge, Sir Eric Geddes, M.P., The Rt. Hon, G. H. Roberts, M.P. roller), Prof. Kirkaldy, W. C. Bridgman, M.P. ary Secretary Board of Trade), Sir William G. J. Wardle, M.P. (Parliamentary Secretary, Labour), and Tom Shaw, M.P. An article on Nations" and "Industrial Unity" is contri- ajor The Hon. Waldorf Astor, M P. There is ccount of the splendid donation of £20,000 by William Dupree towards creating industrial Altogether the Journal maintains its very in- aracter.

CIMAL ASSOCIATION, 212 and 213, Finsbury House, are issuing quarterly an interesting et, "The Decimal Educator." In a circular state:—"There is a general consensus of t the reform in British coinage and weights and ır which we are working should be taken in g the period of reconstruction. To enable us ate public opinion that this object should be e require the help and co-operation of all who ır of our aims, and I hope, therefore, that you ır way to becoming a member of the Decimal . Pamphlets giving the arguments which we l in support of our demand for reform will be to anyone applying for them."

STERN KODAK COMPANY have undertaken the of a very complete series of pure chemicals, e used in photography. The list is very full ply will be of great use to those occupied in ic research. They will probably be available

BLAKE, Assoc.I.E.E., in the *Archives of l Electrotherapy* describes a simple method tatic electricity from an induction coil. A e apparatus used is here given. R is a glass ıg a solution of alcohol and water; it is vo terminal electrodes, Q and K, the latter ed to one of the secondary terminals of an s, its other electrode Q terminates n a blunt point P. The prime conductor of the machine consists of two metal spheres, L and N (about 2 in. diameter), connected to one another by means of a fine wire inductance or choke I; by raising or lowering the resistance tube R, the distance between point P and sphere L can be varied. The inductance is introduced here to damp out any high-frequency oscillations that may be set up. It is well known that such oscillations are always produced when a



spark passes between two eletrodes, they are in fact the origin of Hertzian waves. That this choke has a beneficial effect was actually tested by experiment. It is important to connect the other terminal of the secondary of the induction coil to earth, as shown at E. This has the effect of increasing the intensity of the discharges, and at the same time it helps to prevent the production of inverse current, consequently purer discharges are obtained. In the initial stages of the experiments the secondary terminal of the coil was earthed through a condenser and not directly.

NOTES FROM FOREIGN SOURCES.

Thermic Decomposition of certain Inorganic Trinitrides.—E. Moles.—In 1916 Tiede (*Ber.*, xlix., 1742) published an account of a study of the thermic decomposition of metallic trinitrides in vacuo. He gave the initial temperature of decomposition and that of the regular liberation of nitrogen for the azides of K, Na, Rb, Cs, Ba, Sr, and Ca, and stated that the decomposition is quantitative for all these compounds, the N_2 set free is very pure, and that the metal is deposited in the form of a mirror in the case of the alkaline metals, and as a blackish powder in the case of the metals of the alkaline earths. These results suggested to the author the idea of applying the thermic decomposition of the azides in the revision of the atomic weights of these metals. Values would thus be obtained which were quite independent of that of the atomic weight of Ag, and the value for N would be established with an accuracy exceeding ± 1/14000. He found that the initial temperature of decomposition of AgN_3 is about 300° and that then the gas is evolved very regularly at 280°. But later experiments showed that the decomposition is not as perfect as had been imagined, the weight of the metal obtained by difference being always too great. The value obtained

for sodium were 23·024, 23·086, 23·10. The author is studying the decomposition of NaN_3 and KN_3 and intends to continue these researches on the revision of atomic weights of the metal of the alkalis and alkaline earths.—*Journal de Chimie Physique*, 1918, xvi., 401.

Oxidation of Nitric Oxide by Dry Air.—André Sanfourche.—The reaction between nitric oxide and dry air takes place in two stages, with very different velocities; the first, which is extremely short, corresponds to the formation of nitrous anhydride N_2O_3, while the second and longer stage leads to the formation of peroxide N_2O_4. At the ordinary temperature the velocity of both reactions has been shown by the author and M. P. Jolibois (*Comptes Rendus*, 1919, clxviii., 235) to be not appreciably influenced by the proportion of air. The author has now studied the influence of temperatures lying between $-50°$ and $525°$ upon the same velocity. The results show that the temperature does not appear to have any effect upon the very great velocity of the reaction $2NO+O_2=2N_2O_3$, which is complete in a fraction of a second, but on the other hand it profoundly modifies the course of the reaction $2N_2O_3+O_2+2N_2O_4$ (or $4NO_2$). This reaction, which is also very rapid below 0°, is complete up to about 200°, but occurs more and more slowly, this difference being possibly connected with the dissociation of N_2O_4. Above 200° there is a tendency to establish the equilibrium $2N_2O_3+O_2 \rightleftarrows 4NO_2$. The displacement of the equilibrium takes place from right to left as the temperature is raised from 200 to 600°.—*Comptes Rendus*, 1919, clxviii., 307.

Precipitated Amorphous Silica.—P. Braesco.—Precipitated and calcined silica has usually been known under the name "amorphous silica." The only reason for regarding it as amorphous is that no crystals of definite form can be distinguished, either with the naked eye or under the microscope. But it is well known that similar precipitates, like so-called amorphous barium sulphate, are really crystallised, and the author has investigated the true nature of "amorphous" silica by determining some of its physical properties. Measurements of its dilatation were performed, using Chévenard's apparatus and starting either with silica obtained by the decomposition of sodium silicate with hydrochloric acid, or else with silica obtained by the decomposition of silicon fluoride with water. In both cases the results obtained were the same. When silica is precipitated, dehydrated, and heated only to 600° it behaves exactly like vitreous silica, and has the same low coefficient of dilatation. It is thus true amorphous silica. But when it is precipitated and calcined at a temperature above 1000° there is an abrupt change of dilatation between 220° and 240°, and silica calcined above 1000° is not amorphous silica, but crystallised silica of the cristobalite variety.—*Comptes Rendus*, 1919, clxviii., 343.

Action of Alkalis on Crucibles made of Alloys of Platinum and Gold.—Paul Nicolardot and Claude Chatelot.—These experiments were performed in order to find out whether new platinum is less attacked than old platinum when alkalis are fused with it, and whether the presence of iridium increases or decreases its resistance to the same alkalis. The fusions were all carried out similarly, 5 grms. of alkali being used, and the process occupied ten minutes, the source of heat being a spirit lamp. The crucibles were first weighed, then the fusion was carried out, and they were then washed with water and dried. They were found to have lost weight, and their clean shining surface had been blackened. This black deposit disappears on treatment with hydrochloric acid. The loss of weight of metal is considerable, and is always greater when potash is used than with soda. New crucibles are more resistant than old ones, and the presence of iridium does not increase the resistance, but rather the reverse. The presence of copper does not seem to be as deleterious as that of iridium.—*Bulletin de la Société Chimique de France*, 1919, xxv.-xxvi., 4.

Determination of Zirconium.—Paul Nicolardot and Antoine Reglade.—The formation of a phosphate in an acid medium has been used by Hillebrand to analyse zircons, and it seemed to be of interest to find out whether the precipitation of zirconium is really complete in presence of iron, chromium, and aluminium. The reaction would be characteristic of zirconium, since bismuth, which is very rarely associated with it, is the only element which could be determined in these conditions. The authors have carried out a series of tests to determine the effect of the acidity of the solutions of foreign salts and of the time of contact with the reagents before filtration. The salt used was pure nitrate of zirconium, and the foreign salts added were those of iron, aluminium, and chromium. The results showed that ammonium phosphate in an acid medium (20 per cent at least of sulphuric acid) is a characteristic reagent for zirconium in presence of iron, aluminium, and chromium, and bismuth is the only other element which is precipitated in these conditions.—*Comptes Rendus*, 1919, clxviii., 348.

Cycle of Oxidation of Nitrogen Dioxide in Presence of Water.—André Sanfourche.—The reaction which is generally supposed to take place between nitrogen peroxide and water can be represented by the equation $3N_2O_4+2H_2O=4HNO_3+2NO$. The study of the velocity of oxidation of nitrogen dioxide, however, suggests that nitrous anhydride may play some part in the reaction, and this hypothesis can be verified by bringing into intimate contact vapour of nitrogen peroxide mixed with an excess of air and water or more or less diluted nitric acid. The experiments show that in the oxidation of nitrogen dioxide in presence of water nitrous anhydride is the intermediate product and not nitrogen peroxide. Nitrous anhydride is oxidised by nitric acid of sufficient concentration with formation of nitrogen peroxide and water this reaction is limited by the inverse reaction. Thus there must be equilibrium for a certain concentration of nitric acid, and experiments show that this concentration is in the neighbourhood of 50 per cent.—*Comptes Rendus*, 1919, clxviii., 401.

Substitutes for Platinum in Electrolytic Apparatus. Paul Nicolardot and Jean Boudet.—Metals or alloys which are to be used to replace platinum in electrolytic apparatus must be unalterable even in moist warm air containing sulphuretted hydrogen. They must be able to be washed with water and dried without change of weight, and must resist the action of pure nitric acid. They must remain unaltered during electrolysis in the liquids generally employed—sulphuric and dilute nitric acids, dilute ammonia, aqueous solutions of sodium sulphide and cyanide. They must also possess the mechanical qualities necessary to enable them to be worked up into the usual shapes of electrodes. Various commercial alloys have been investigated by the authors for the purpose, and they have found that the most suitable is an alloy of gold containing—gold, 920 parts; silver, 50 parts; copper, 30 parts. It is very resistant towards nitric acid. In the case of the anode the surface must be covered with a very thin layer of platinum (0·005 grm. per square cm.) by electrolysis, to protect it against oxidation. The alloy can be used as such for the cathode.—*Bulletin de la Société Chimique de France*, 1918, xxiii.-xxiv., 387.

MISCELLANEOUS.

Atoms, Electrons, and Valency.—With the more recent views of the disintegration of matter, chiefly the result of the discovery of radium, the electro-positive and negative character of the elements come into play. The constancy of mass and weight are involved in their disintegration, and a dual variable electric character might

be ascribed to the elements. With regard to mass the measure of which is weight the force of gravity, there is still needed an efficient theory of this force, and, admitting the disintegration of matter, such factors as atomic heat and gas volumes are more the essential properties of the atoms. If the atomic weights are considered in relation to the periodic law, most attention has been given to the relationship existing in the several groups. The increase of atomic weight in the horizontial period may have some relation to valency, and in the latter half of the periodic table the halogens which, classed as heptads, are monovalent with the alkali metals in the first half, valency being a more complex function of the constitution of the elements. Taking the increase of atomic weight as affecting valency, in the periods and the group relationship as to weight, atomic volumes introduce the conception of space. The views of the disintegration of matter may be advanced not only by considering the radium elements but ionisation in liquids and the electric discharge in rarefied gases.—J. C. Thomlinson.

Geological Society.—At the Annual Meeting, held February 21, the following Medals and Awards were presented:—

Sir Aubrey Strahan, K.B.E.—The Wollaston Medal.

Miss Gertrude L. Elles, Sc.D.—The Murchison Medal.

William Fraser Hume, D.Sc.—The Lyell Medal.

Major Sir Douglas Mawson, D.Sc.—The Bigsby Medal.

Alexander Logie Du Toit, D.Sc.—Balance of the Proceeds of the Wollaston Donation Fund.

Mrs. Eleanor M. Reid, B.Sc.—Balance of the Proceeds of the Murchison Geological Fund.

Mr. John Pringle.—Moiety of the Balance of the Proceeds of the Lyell Geological Fund.

Stanley Smith, D.Sc.—Other moiety of the Balance of the Proceeds of the Lyell Geological Fund.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The decease of Sir James Mackenzie Davidson, a Member and a Manager of the Royal Institution, was announced, and a Resolution of Condolence with Lady Mackenzie Davidson and the Family was passed. Miss A. Campbell, Dr. C. B. D Campbell, Mrs. E. H. Campbell, Mr. J D. Campbell, Mr. R. G. Campbell, Mrs. E. Davies, Miss H. M. Douglas, Mr. G. K. B. Elphinstone, Mr. J. W. Evans, Mr. C. W. Hawksley, Captain A. J. Hoillck, Lord Leigh, Miss I. H. Mond, and Mr. R. A. Yule were elected Members.

Oxygen a Revolutioniser of Industry.—(From the *Technical Supplement*, Feb. 18).—Due to the rapid growth of the nitrate industry based on the fixation of atmospheric nitrogen, the cost of oxygen has fallen enormously since the outbreak of the war. This great achievement in science, whereby oxygen is made a by-product of an important manufacture, is likely to work a revolution in industry. The uses of oxygen, when cheaply produced, are almost endless. Gas manufacturers will not be slow to utilise it to increase the light of their burners where a strong illumination is required; for that purpose new forms of burners will be called for. In metallurgical operations a small percentage of oxygen blown into the furnaces will raise the temperature considerably. In such cases it will allow inferior and cheaper qualities of coal to be used. Carbide of calcium will be produced in the blast-furnace by a purely thermic method. Alumina will be reduced by carbon. Auriferous quartz will be melted. The glass industry will be revolutionised by the easy fusing of all forms of quartz. A new chemistry, viz., that of the electric furnace, will be created. The manufacture of sulphuric acid will be much accelerated by the powerful oxidation of sulphurous acid. The production of ozone, or electrified oxygen, opens up numerous vistas, notably for the sterilisation of drinking water and the maintenance of a wholesome atmosphere in factories, workshops, schools, theatres, barracks, hospitals, underground railways, and mines. For use in mines it may be of inestimable service.—*Bulletin de la Societé de l'Industrie Minérale*, Third Issue, 1918.

MEETINGS FOR THE WEEK.

Monday, 14th.—Ceramic Society, 7. (In the Central Schools of Science and Technology, Stoke-on-Trent). "Substitution of Apatite for Bone-ash in the Bone China Body," by N. B. Davies. "Heat Conductivity of Porous Materials and the Heat Insulation of Kilns," by J. W. Mellor. "Casting of Heavy Pottery," by B. J. Allen.

Tuesday, 15th.—Institution of Petroleum Technologists, 5.30. "Some War Problems of Petroleum Supply," by Sir Frederick W. Black.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3079.

SOME AMERICAN DOLOMITES.

By BURLEIGH B. REED.

THESE rocks are among the important building stones of the country and have a wide distribution. We secured a few typical specimens from different sections in order to make a comparison of their chemical composition. The specimens analysed are all used as building materials in their respective localities.

1. From Mount Vernon, Iowa, and belongs to the Niagara formation, the oldest member of the Silurian age. It is hard and compact, and has a yellowish tint due to the presence of iron. Analysis as follows:—

	Per cent.
SiO_2	1·29
Fe_2O_3 and Al_2O_3	0·57
$CaCO_3$	55·17
$MgCO_3$	43·04
Total	100·07

2. Dolomite from Westchester County, New York, not far from New York City. It is a white crystalline rock, and is a coarsely granular marble in appearance. The formation belongs to the Cambro-Silurian, and is thought to be equivalent to the Stockbridge limestones of the Housatonic Valley in Massachusetts. It is quite a typical dolomite in composition, not materially different from the Iowa rock. The analysis as follows:—

	Per cent.
SiO_2	2·71
Fe_2O_3 and Al_2O_3	1·05
$CaCO_3$	53·43
$MgCO_3$	42·93
Total	100·12

3. From Lockport, New York, also belonging to the Niagara formation. There was upon the dark grey rock an incrustation of milk-white crystals. The analysis of the body of the rock, which was hard and compact, resulted as follows:—

	Per cent.
SiO_2	2·76
Fe_2O_3 and Al_2O_3	1·42
$CaCO_3$	51·85
$MgCO_3$	43·94
Total	99·97

The specimen contains a sufficiently high percentage of magnesium to class the rock as a fairly typical dolomite.

4. The white crystals encrusting the specimen:—

	Per cent.
SiO_2	0·18
Fe_2O_3 and Al_2O_3	1·21
$CaCO_3$	81·62
$MgCO_3$	17·15
Total	100·16

This varies quite widely from a true dolomite as the calcium has largely replaced the magnesium. The amount of silica is unusually small, as might possibly be expected from the crystalline structure of the material.

5. From Bertram, Iowa. This belongs to the Niagara formation which lies between Mount Vernon and Cedar Rapids. The rock is grey in colour with numerous small light coloured crystals disseminated through the msss. Some analytical data had been found which seemed to indicate that the magnesium content of the rock was in excess of the calcium. Our analysis was made with a view to determine whether this was really the case. Two concordant results obtained are as follows:—

	Per cent.
SiO_2	0·90
Fe_2O_3 and Al_2O_3	0·90
$CaCO_3$	55·61
$MgCO_3$	42·58
Total	99·99

The figures indicate a rather typical dolomite, as one would naturally expect from the analysis of similar specimens in the neighbourhood.

The analyses were made by the methods outlined in the revised edition of Knight's "Quantitative Analysis."

Cornell College, Mount Vernon, Iowa,
March 17, 1919.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

(Concluded from p. 173).

THE validity of the foregoing equation being thus established it may be employed to calculate for even temperatures and a number of pressures the maximum quantities of ammonia obtainable by the interaction of nitrogen and hydrogen. These figures, constituting a summary of the influence of temperature and pressure on the ammonia equilibrium, are presented in the following table [valid for 1 vol. nitrogen + 3 vols. hydrogen]:—

Temp. cent.	Equilibrium percentage of ammonia at— 1 atmo.	30 atmos.	100 atmos.	200 atmos.
200°	15·3	67·6	80·6	85·8
300°	2·2	31·8	52·1	62·8
400°	0·44	10·7	25·1	36·3
500°	0·129	3·62	10·4	17·6
600°	0·049	1·43	4·47	8·25
700°	0·022	0·66	2·14	4·11
800°	0·002	0·35	1·15	2·24
900°	0·0069	0·21	0·68	1·34
1000°	0·0044	0·13	0·44	0·87

From the physico-chemical standpoint then the conditions which affect the position of the ammonia equilibrium are thoroughly understood, and their influence can be definitely formulated. Plainly, the highest percentage conversion of nitrogen and hydrogen into ammonia is to be secured by working at a high pressure and a low temperature. There is, however, a limit to the pressure under which a large scale process can be carried out conveniently and safely, and the pressure employed in practice is not above 150—200 atmospheres. The use of high pressures such as those just quoted leads not only to a favourable displacement of the equilibrium, but also to an increased rate of approach to the equilibrium position.

* Cantor Lecture (I.). Delivered before the Royal Society of Arts, December 2, 1918. From the *Proceedings of the Royal Society of Arts*, xvii., No. 3450.

A limit is set also to the reduction of temperature, which from the point of view of yield alone is desirable, by the difficulty of finding catalysts which are sufficiently active below 500—600° C. From the point of view of technical production the rate at which the reaction takes place is naturally of prime importance, and this comes back really to the question of the activity of the catalyst employed.

Of itself the reaction $N_2+3H=2NH_3$ takes place very slowly at temperatures below 1000°, and it is only in the presence of catalysts, such as osmium, uranium, and iron, that the formation of ammonia becomes reasonably rapid at temperatures where the yield is still moderately satisfactory. In the manufacturing process a mixture of nitrogen and hydrogen at a pressure of 150—200 atmospheres is passed over the catalyst at a temperature of 500—600° C., the small quantity of ammonia formed is removed by refrigeration or absorption, and the residual gases are again circulated over the catalyst. High yield and rapid establishment of equilibrium are not reconcilable, and a balance has to be struck at the temperature which gives the best economic results.

In working out the most satisfactory conditions for the technical synthesis another factor has to be considered, and that is the rate of circulation of the gases over the catalyst. If this rate is high the percentage of ammonia formed per passage will fall a good deal short of the equilibrium percentage, but, on the other hand, there will be all the more passages in a given time. It has, indeed, been shown by Maxted that for a catalyst chamber of given size the highest yield of ammonia per hour is obtained with a very high rate of circulation and a minimum value for the percentage of ammonia formed per passage. This is made clear by the following record, obtained with an iron-potash catalyst at 550° C. and 150 atmospheres:—

Time of contact of gas with catalyst in seconds.	Per cent ammonia formed.	Yield of ammonia in kilos per hour per litre of catalyst space.
0·34	0·65	2·7
0·56	0·94	2·3
1·8	1·8	1·4
3·6	3·2	1·25
7·2	4 7	0·91

From recent information, for which the writer is indebted to Mr. Maxted, it appears that with a somewhat more active iron catalyst and extremely rapid circulation, yields of ammonia up to 10 kilos per hour per litre of catalyst space may be obtained. There are, however, difficulties in the construction of satisfactory heat exchangers for the commercial utilisation of such rapid circulation. The optimum rate of circulation must be determined for each plant.

The fact that in actual working, where a moderately high rate of circulation is employed, the percentage of ammonia does not reach the equilibrium value, involves the possibility that a rise of temperature may even lead to an increase in the yield of ammonia per passage. This has been found to occur in some experiments carried out by Maxted at 530° and 580° C.

Catalyst—iron potash. Time of contact in seconds.	Pressure—150 atmos. Percentage of ammonia formed at—	
	530°.	580°.
0·6	0·96	1·5
1·0	1·3	2·4
1·5	1·7	3·2
2·0	2·05	3 8

Such an increase in the yield accompanying a rise of temperature can occur only when the yield is much less than the maximum obtainable—*i.e.*, the equilibrium value. At a higher range of temperature, where the establishment of equilibrium is very rapid, a rise of temperature will lead to a decrease, not an increase, of the ammonia yield.

It has been shown above that the displacement of the ammonia equilibrium with rise of temperature is represented by the equation—

$$\log_{10} K = \frac{2098}{T} - 2{\cdot}5088 \log_{10} T - 0{\cdot}0001006\,T + 0{\cdot}186 \times 10^{-6}\,T^2 + 2{\cdot}1,$$

and the values of K given by this formula are in good agreement with the figures obtained experimentally up to 1000° C. If the validity of the formula is assumed for still higher temperatures it follows, as shown by Maxted, that the decrease of K with rising temperature continues up to a point about 2500° abs., but that a further rise of temperature should be accompanied by an increase of K. The approximate position of K appears from the following calculated figures:—

T° abs.	$K \times 10^4$.
1500	0 63
2000	0·26
2500	0·21
3000	0·28
3500	0·55

It should be noted that where the displacement of equilibrium with rising temperature is reversed, the heat effect of the reaction must pass through a zero value. This follows from the thermodynamic equation—

$$\frac{d(\log_e K)}{dT} = -\frac{Q}{RT^2}.$$

The prediction of an increased yield of ammonia at extremely high temperatures, a prediction based, it must be admitted, on a very extensive extrapolation of the formula for K, has been verified by Maxted's experiments. In these a mixture of nitrogen and hydrogen was introduced into an oxy-hydrogen flame, and then cooled with extreme rapidity to the ordinary temperature. The gas was then found to contain appreciable quantities of ammonia, estimated in one case to be equivalent to 1·23 per cent by volume at an absolute pressure of one atmosphere. Rapid cooling is essential, otherwise the equilibrium shifts to the unfavourable position characteristic of the temperatures between 1500° and 3000° abs. The passage of a nitrogen + hydrogen mixture through a capillary tube in which a small high-tension arc is burning leads also to the formation of appreciable quantities of ammonia. It will be interesting to see whether this thermal synthesis of the gas can be effected on anything else than the very small scale which has so far proved practicable.

The catalytic synthesis of ammonia at moderate temperatures, on the other hand, has come rapidly to the front, and has played no small part in the war technology of Germany, where the process was being developed on the large scale in the period 1912-14. During the war synthetic ammonia was turned out in that country at a rapidly increasing rate, and it is stated that the quantity of ammonium sulphate produced by this method has recently amounted to about half a million tons per annum. The significance of this synthetic ammonia industry lies in the fact that the product can be readily oxidised to nitric acid, which, of course is the indispensable basis of explosives. The fixation of atmospheric nitrogen, however, will be required to meet the needs of peace also, in respect of nitrogenous fertilisers, and in all probability the catalytic synthesis of ammonia has a future before it independent of the demands of war.

In final illustration of the value of the principles of chemical equilibrium in the rational survey and control of a technical gas reaction, one or two points connected with the water gas reaction $CO_2+H_2 \rightleftarrows CO+H_2O$ may be discussed. There are an equal number of molecules on the two sides of this equation, and it therefore follows that

a shift of the equilibrium involves no change of volume. Hence in conformity with Le Chatelier's principle already referred to, an alteration of the pressure is without effect on the position of equilibrium.

The equilibrium constant in this case is defined as $K = \frac{c_{CO} \cdot c_{H_2O}}{c_{CO_2} \cdot c_{H_2}}$, where c_{CO}, c_{H_2O}, c_{CO_2}, and c_{H_2} are the equilibrium concentrations of the different gases concerned. The reaction being reversible it is possible to approach the equilibrium from either side, and in the actual investigation of the reaction the value of K was deduced from two sets of experiments—(*a*) those in which mixtures of carbon dioxide and hydrogen were passed through a heated quartz or porcelain tube containing platinum as a catalyst; (*b*) those in which mixtures of carbon monoxide and water-vapour were treated similarly. An analysis of the gas mixture issuing from the tubes gave the values of the equilibrium concentrations. As an example of the results obtained under (*a*) the following, recorded at 986° C., may be quoted :—

Percentage Composition of the Initial Mixture.

CO_2.	H_2.
10·1	89·9
30·1	69·9
49·1	51·9
60·9	39·1
70·3	29 7

Percentage Composition of the Equilibrium Mixture.

CO_2.	$CO=H_2O$.	H_2.	K.
0·70	9·46	80·38	1·59
7·18	23·00	46·82	1·58
21·36	27·88	22·88	1·59
34·20	26·61	12·58	1·64
47·66	22·79	6·76	1·61

Experiments carried out at the same temperature with initial mixtures of carbon monoxide and water-vapour gave a mean value of 1·55. The agreement of this number with the average of the figures for K recorded in the table shows that the equilibrium between the four gases, whatever their initial concentrations, is established in conformity with the mass action law.

As regards the shift in the equilibrium with rise of temperature the direction of the shift can be deduced from the known heat effect of the reaction $CO_2+H_2=CO+H_2O$. At the ordinary temperature the occurrence of this reaction from left to right is accompanied by the absorption of about 10,000 calories, and hence a rise of temperature will favour the system $CO+H_2O$ at the expense of the system CO_2+H_2. Quantitatively this is shown by the increasing values for K obtained with rising temperature. Thus the figures for the constant at 686°, 786°, 886°, 986°, and 1086° are 0·53, 0·84, 1·20, 1·57, and 1·96 respectively.

The water gas equilibrium is of interest in relation to the manufacture of hydrogen, the demand for which has steadily increased during the last five or ten years. Apart from its use in connection with airships and balloons, there are various newer industries, in which the gas is required on a large scale, as, for example, in the hardening of fats and in the synthetic ammonia industry. Among other methods for the manufacture of hydrogen in quantity it has been found possible to make the hydrogen of water available by first producing water gas, and subsequently passing the water gas with excess of steam over a catalyst, such as alkaline ferric oxide, at a temperature of 500—600°. The raising of the concentration of the water-vapour must plainly shift the equilibrium in the reversible reaction $CO_2+H_2 \rightleftharpoons CO+H_2O$ over towards the left, and in actual practice it is found that the carbon monoxide of the water gas is almost completely converted into carbon dioxide by this treatment, and that there is a corresponding increase in the quantity of hydrogen. Thus, in one case on record, a water gas containing 24 per cent carbon monoxide was found, after one passage over the catalyst at 500° with excess of steam, to contain only 2 per cent of this gas. Naturally the carbon dioxide and the residual carbon monoxide must be removed by condensation or absorption if pure hydrogen is required.

MECHANICAL PHILOSOPHY AND THE SECOND LAW OF THERMODYNAMICS.

By FRED. G. EDWARDS.

THE atom of the ether is a tetrahedron of mass one-fourth of the hydrogen molecule ($3\cdot2\times10^{-24}=0\cdot8\times10^{-24}$ grm., and assuming the specific density of the ether determined below at 0·575 its atomic volume will be $1\cdot39\times10^{-24}$ cc. equal to a sphere of diameter $1\cdot39\times10^{-8}$ cm. Its atomic domain is defined by an ascribed rhombic dodecahedron, but as each atom collides with four only of the twelve contiguous atoms the whole formation is divided into two interpenetrating plena. The specific density D of the ether may deduced as a first approximation at 0·575 from the formula $R=R_1(D/D_1)^{\frac{1}{3}}$, where R_1 is the refractive index ($=2\cdot4669$), and D_1 the density ($=3\cdot5$) of diamond, and $R=1$. The pressure of the ether is now directly deduced at 5175×10^{17} dynes per sq. cm. from the radiation velocity by the formula $c=(p/d)^{\frac{1}{2}}$, where $c=3\times10^{10}$ and $d=0\cdot575$.

It has, perhaps, been too readily assumed that an atomic ether besides a density and a pressure must also have a temperature; but the real physical interpretation of the second law of thermodynamics for solids and liquids will now be deduced in terms of atomic motion. To the above formula may be added a ratio-factor, thus $a=(pk/d)^{\frac{1}{2}}$, where $k=1$ in the case of light travelling through a frictionless ether. But in the case of sound in ethyl-ether-vapour the ratio of the specific heats $k=c_p/c_v=1\cdot06$, and the reciprocal ratio h of the intramolecular energy over the rectilinear molecular energy deduced from the thermodynamic formula $h=(5-3k)/(3k-3)$ is 10. This means that if there be one quantity-intensity unit of atomic energy, radiating or absorbing heat evidenced as temperature, there are ten other quantity units of energy in the form of intramolecular motion. The energy of this non-radiating motion is pure entropy. But when $k=1$ then $h=\infty$, or the whole of the energy is entropy, and there is no temperature, as the intensity factor $=0$. This is the limiting condition for solids and liquids, but is inapplicable to gases where the free energy is molecular and the size of the molecule is not infinite as in the former cases.

The hydrodynamic pressure of the ether on a circular area of diameter $5\cdot3\times10^{-11}$ cm. would be 41·8 dynes, and if two spherical cavities at one diameter apart centre to centre mutually repel with this force their repulsion at 1 cm., inversely as the distance squared, would be $1\cdot17\times10^{-19}$ dynes as against $1\cdot16\times10^{-19}$ dynes in the case of electrons. Only by such a structure would a massless electron remain in a material universe. The diameter is less than 10^{-2} times that of the calculated ethereal volume, so that its formation by the removal of a "positive" atom involves four tetrahedrally inclined strains in the ether, corresponding to the lines of force, which on a conductor would be reduced to one free line or tube of force. The electron theory is true, but it is a developed negative from which a positive picture should be formed.

The mathematical theory of electro-dynamics is a special form of the theory of elasticity. The electrical work done by a planet moving through an apparently stagnant ether reappears as energy in gravity. The centripetal radiations of gravity are the cause of apparent

irrelativity, and also the source of the sun's energy now admitted to be 10^8 times greater than can be otherwise accounted for. The quantum is a function of atomic mass, and should be the momentum of an atom as it strikes the ether in striking an electron, and Planck's constant would be the unit action of the ether in the formation of waves.

Radiation is thus energy in the form of momentum travelling through a material fluid as visualised by Maxwell, but he was not bold enough to deduce the density and pressure of the medium by the ordinary laws of mechanics, doubtless because at that time he considered the first law of dynamics applicable to produce temperature. Stokes, Kelvin, and Helmholtz have shown that direct action at a distance, now exclusively used in electrical theory, is mathematically identical with the action of an incompressible fluid. That fluid, which formed the foundation of his great electrical theory and which he repeatedly insisted upon, is now specified with its electronic displacement.

March 29, 1919.

ARSENIOUS OXIDE AS A STANDARD SUBSTANCE IN IODIMETRY.

By ROBERT M. CHAPIN.

Introduction.

Following the development of a reliable laboratory method (*Journ. Ind. Eng. Chem.*, 1918, x., 522) for the preparation of pure arsenious oxide, an investigation has been made of the accuracy possible when the substance is employed in iodimetry. Though the process has long been in common use it seems never to have received the rigorous testing demanded by modern standards. The work of Washburn (*Journ. Am. Chem. Soc.*, 1908, xxx., 31) extended merely to a study of the precision possible, that is, the closeness of agreement among titrations. The work here presented involves the direct comparison by titration with weight burettes, of known amounts of pure arsenious oxide and pure iodine. The object was to establish the reliability of properly purified arsenious oxide as a standard to replace the less convenient iodine which has been the final recourse in work calling for the highest possible degree of accuracy. This substance is the simple oxide of an element of very accurately determined atomic weight; it is non-hygroscopic, permanent in the solid state, and also highly permanent in a properly acidified solution.

Preparation of Pure Substances.

Arsenious oxide was obtained in the form of a coarse powder nearly free from dust by resubliming some material purified in the manner already referred to. (The raw material comprised several grades; chiefly "technical" white arsenic).

Pure iodine was obtained by a process abridged from that of Guichard (*Ann. de Chim.*, 1917, vii., 27). Potassium iodide U S P., 100 parts, and iodine U.S.P., 150 parts, were dissolved in water, 100 parts. To the solution was added about 5 parts crystallised copper sulphate in warm concentrated solution. After thorough stirring and standing for some time the precipitate was filtered off and the filtrate distilled from a retort into a cooled flask, water being added as necessary. The iodine in the distillate was filtered with suction on a hardened paper in a Buchner funnel, washed with water, and redistilled with water from the same apparatus. After again filtering, washing and draining, it was thoroughly dried over calcium chloride, then sublimed twice with intermediate drying. The subliming apparatus consisted of a shallow beaker, on the rim of which rested a globular flask filled with cold water. During the second sublimation the substance was not collected until a liberal preliminary portion had been allowed to escape, and it was obtained in loose crystals by frequent removal from the condensing flask. It was finally ground to coarse powder in a glass mortar, and preserved over calcium chloride.

Preparation of Solutions.

The solution of arsenious oxide in dilute sulphuric acid, as recommended by Roark and McDonnell (*Journ. Ind. Eng. Chem.*, 1916, viii., 327) appears for obvious reasons the safest method of preparation. The only question is the possible volatilisation of an appreciable quantity during the necessary boiling, and therefore the following experiment was conducted.

Experiment 1.—In a side-tube distilling flask was placed 5 cc. concentrated H_2SO_4 in 300 cc. H_2O. Flask and condenser were fitted with bark corks. The distillate, collected in portions of 25 cc. and tested for arsenic in a modified Gutzeit apparatus, yielded a very low blank. To the remaining 200 cc. liquid in the flask was then added 2½ grms. As_2O_3, and distillation was resumed, successive portions of 25 cc. being taken off while the volume in the flask was maintained at 100 to 200 cc. All portions collected except the first, which contained less, owing to delayed solution of the substance, showed a constant content of 20 micromgrms. As_2O_3. Finally the condenser tube was filled with 50 cc. diluted H_2SO_4 and left one-half hour. No more As_2O_3 was found in this solution than in the blank.

Therefore, in the preparation of one litre of tenth-normal arsenious oxide solution it would be necessary to boil off more than 600 cc. in order to diminish the strength of the finished solution by 1 part in 10,000. (Since hardly a fourth of the above proportion of liquid need be lost through gentle boiling in a long-necked volumetric flask, any such additional precaution as a reflux condenser, which has been suggested as an absolute preventive against loss, is obviously superfluous).

About 0·8 grm. dry arsenious oxide was weighed out by difference from a vial into a weighed 100 cc. volumetric flask. To avoid loss of dust the vial was chosen small enough to slip easily within the neck of the flask during transference of the substance. Solution was effected by very gentle boiling in a mixture of 16 cc. of dilute sulphuric acid (1 in 10) with about 60 cc. water. Water was then added to the cooled solution up to the base of the neck of the flask and a second weighing was made.

For weighing the iodine, ampules were prepared by blowing a bulb of slightly less than 2 cm. diameter on the end of a glass tube of 5 mm. bore, which was further drawn down to about 2 mm. at 1 to 2 cm. above the bulb, and lastly cut off to a total length of about 11 cm. Into the bulb of this miniature flask was charged through a slender tube 1·5 cc. of a solution of C.P. potassium iodide (10 grms. per 15 cc.) without wetting the interior of the apparatus above the constriction. After the weight, constant on the balance for ten minutes, had been ascertained, about 0·8 grm. iodine was introduced, most of which remained above the constriction. The tube was drawn out above the iodine to a capillary, which, after cooling to room temperature over calcium chloride, was sealed off by a small blow-pipe flame. The tip thus separated was gently heated to remove condensed iodine, and finally, after cooling, the weight of tube *plus* tip, constant for ten minutes, was ascertained, and consequently the weight of iodine obtained. A tube treated in a similar way, except that no iodine was added, showed a variation in weights before and after sealing decidedly less than 0·1 mgrm.

All weights, including burette readings, were reduced to vacuum and the weights of the two substances themselves were further corrected by means of the Bureau of Standards certified corrections for the set of weights employed.

The water used was freshly collected from a large laboratory still of a modern type which delivers water substantially free from dissolved gases. All solutions were employed shortly after preparation.

Execution of the Titrations.

In the ordinary titration of arsenious oxide with iodine, sodium bicarbonate is the buffer usually employed to maintain neutrality and is entirely appropriate for the purpose. For the reverse titration here contemplated it presented obvious defects. The sodium phosphate mixture advocated by Washburn appears to react with inconvenient slowness. A borax-boric acid mixture was also stated by Washburn to be theoretically applicable but was not regarded by him as practically so useful as phosphate or bicarbonate. Barneby (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 330) found such a mixture useful in "differential iodimetry." It effects a rapid reaction and is otherwise entirely convenient. The proportion of boric acid necessary to prevent the formation of iodate was determined by the following experiment:—

Experiment 2.—To 50 cc. of a solution containing recrystallised $Na_2B_4O_7 10H_2O$, with or without H_3BO_3, was added 50 cc. N/20 I. After standing twenty-two hours an excess of H_3BO_3 was added and the solution was titrated with $Na_2S_2O_3$ (N/100 at end) and starch. Then diluted HCl was added in excess and the liberated iodine titrated with N/100 $Na_2S_2O_3$.

Table I.—*Formation of Iodate in Presence of Borax and Boric Acid.*

No.	$Na_2B_4O_7.10H_2O$. Grms.	H_3BO_3. Grms.	N/100 $Na_2S_2O_3$. Cc.
1.	0	0	0·00
2.	5	0	9·15
3.	5	1	1·90
4.	5	2	0·10

It appears, therefore, that a buffer solution containing borax and boric acid in the weight ratio of 2 to 1 may be used with entire safety as respects formation of iodate. The solution adopted contained 8 per cent of crystallised borax and 4 per cent boric acid.

With this fact established the following experiment was carried out to test the accuracy of the method—

Experiment 3.—A tube of iodine, thoroughly shaken to dissolve all the substance, was placed in a stout 500 cc. bottle of clear glass, to which was also added 30 cc. of a freshly prepared 10 per cent solution of pure potassium iodide and 125 cc. of the buffer solution. After cooling the whole to about 10° C., the tube of iodine was shattered by pressure with a stout glass rod and an arsenious oxide solution was run in from a weight burette to decoloration. After adding 2 cc. of freshly prepared starch solution the final end point was reached by cautious titration with N/100 iodine (see Note 1). For the blank (see Note 2) another bottle was charged with 40 cc. potassium iodide solution, 125 cc. buffer solution, 2 cc. starch and water to equalise volumes, and the mixture cautiously titrated with the N/100 iodine solution until the colours in the two bottles matched. The volume of N/100 iodine needed for titration of excess arsenious oxide was in no case more than 2 cc. and for the blank never more than 0·2 cc. The colours were not significantly affected by further addition of the buffer mixture, nor by longer standing. The results calculated from the titrations appear in Table II., under Tests No. 1 to 4.

After this work had been completed there appeared a paper by McCrosky (*Journ. Am. Chen. Soc.*, 1918, xl., 1662) in which it was stated that perfectly dry iodine was obtained only by fusion in the weighing tube, a procedure which affected his results by more than 1 part in 700. In contrast with McCrosky the present writer had not passed a continuous current of cold water through his subliming apparatus and had noted no condensation of moisture thereon, while in the final sublimation the substance was collected only after considerable heating, possibly only after complete fusion. But the uncertainty necessitated further work. The following experiment was therefore carried out:—

Experiment 4.—In a 2 cc. glaes-stoppered weighing tube about 0·8 grm. iodine was fused as described by McCrosky and, after weighing, the tube with loosened stopper was dropped into a 500 cc. funnel-necked glass-stoppered Erlenmeyer flask containing 7 cc. of 40 per cent potassium iodide solution. Into the funnel around the stopper was poured 3 cc. of the potassium iodide solution, and after all iodine had been dissolved, this, followed by 125 cc. of borax buffer, was allowed to flow down the sides of the flask. The titrations were made as previously described and the results are given in Table II. under Tests 6 and 7. Test 5 was made without fusion on a sample of the original iodine which had been contained in a glass-stoppered weighing bottle resting in a dark cabinet during seven months.

Table II.—*Comparison of Iodine and Arsenious Oxide.*

No.	As_2O_2 sol.	Weigh I. / Weight As_2O_3.
1.	A	2·5664 (*a*)
2.	A	2·5657
3.	B	2 5661
4.	B	2·5658
5.	C	2·5656
6.	C	2·5661
7.	D	2·5656
Average ratio determined ..		2·5658
Theoretical ratio by 1918 official atomic weights ..		2·5651
Difference		0·0007

(*a*) Excluded in computing average.

Evidently the original iodine was perfectly dry, and pure iodine is not hygroscopic. Evidently, too, the cumbersome method of weighing employed in the first four tests offers no advantage over the use of a stoppered weighing bottle with proper precautions. Fusion before weighing, though unnecessary in the present case, is certainly a desirable precaution. Excluding the unsubstantiated result of Test 1, the greatest variation of any test (No 3 and No. 6) from the average was therefore 1 part in 8500, while the average of the observed ratios differed from the theoretical ratio by less than 1 part in 3600. The difference is in the direction which indicates a less purity, or a greater loss during manipulation of the iodine, and consequently is in favour of arsenious oxide as the more reliable standard in practice.

Precautions in the Preparation and Use of Standard Iodine Solutions.

Aside from correct standardisations, iodine solutions intended for accurate work demand some special precautions previously known in a general way but rarely observed. The first of these is the use of potassium iodide in quantity sufficient not merely to dissolve the iodine in concentrated solution but to inhibit dissociation of potassium tri-iodide, and consequent ready volatilisation of iodine after dilution to standard strength. The proportion of double the weight of iodine in twentieth-normal solutions authoritatively recommended is unquestionably too low (*Journ. Assoc. Official Agr. Chemists*, 1916, ii.; "Report of Comm. on Edit. Meth. of Anal.," p. 63), for loss of strength during a series of titrations with such a solution as ordinarily manipulated may be readily demonstrated. Since potassium iodide is a high-priced substance each worker must decide for himself what proportion the character of his work warrants him in using. The writer has adopted the proportion of 4 per cent in both tenth-normal and twentieth-normal solutions in which a high degree of accuracy and permanence is desired.

The presence of iodate in an iodine solution may naturally cause variation in its apparent strength according to whether titrations are conducted in a neutral or acid

medium. Though commercial potassium iodide appears generally to be free from iodate there are some grounds for the suspicion that iodate may be formed in iodine solutions under certain conditions of storage (Deiss, *Chem-Ztg.*, 1915, xxxviii., 413). It may be tested for by the procedure described under Expt. 2, and if present may be removed by addition of the corresponding amount of sulphuric acid.

A final precaution is to attain the end-point with starch at a temperature not above 25° C. It is well enough known that the blue colour of iodised starch disappears completely on slight heating, but in fact warming even to 30° C. is sufficient to affect distinctly the delicacy of the end-point.

Summary.

It was found that by employing weight burettes with appropriate precautions, six titrations of pure arsenious oxide against pure iodine gave highly precise results, the average of which agreed within 1 part in 3600 with the theoretical value. The evidence is in favour of arsenious oxide as the more reliable standard substance in practice. Precautions in the preparation and use of standard iodine solutions are emphasised.—*Journal of the American Chemical Society*, xli., No. 3.

Notes.

1. The starch solution contained 0·5 per cent potato starch, boiled two hours with water, plus 3 per cent boric acid added towards the end of the boiling period. A briefly boiled starch solution is revealed under a magnifying glass as a suspension of enormously swollen granules. When such a solution is used as an indicator the resulting colour is located partly in the granules and partly in the medium; not an ideal condition if delicacy of end-point is a paramount consideration. Though still visible after a half-hour, granules can no longer be detected after one hour of boiling, while boiling for an additional hour appears to effect no further change. Long boiled solutions are equally as sensitive as solutions boiled only two minutes. The tints afforded with minimal amounts of I are likewise entirely comparable, ranging from pure blue through violet to rose as the concentration of KI and other salts is increased. Boric acid, not previously used as a preservative for starch solutions so far as the writer is aware, appears to be very effective against moulds, though not against salivary enzymes. Solutions used intermittently during several months, and closed only by a pipette or inverted beaker, appear indistinguishable from fresh solutions. In contrast solutions of soluble starch prepared by acid hydrolysis soon suffer degradation.

2. The truth of the blank obtained by this procedure has been questioned. In the first place, making the justifiable assumption that NaI produced from 0·8 grm. I will exert exactly the same effect upon the end point as an equivalent amount of KI, particularly in the presence of a preponderating amount of the latter salt, it will be noted that the equivalent of 4·04 grms. KI was present in the regular run against 4·0 grms. in the blank. Secondly, the volumes of buffer and starch solutions were the same, while the colours were matched at equal final volumes. From previous experience assurance was felt that, provided equal concentrations of KI and approximately equivalent concentrations of total salts were maintained in order to equalise the salt effect upon the end-point, no specific effect would be produced by the minor differences in composition which existed. On the contrary it was feared that far greater risks of error would be incurred through the introduction of extraneous substances in an attempt to make the composition of the solutions exactly similar. But the possible magnitude of error in the blank has now been investigated. To a "true" blank should be added HI derived from 0·8 grm. I, As_2O_5 derived from 0·312 grm. As_2O_3 and 6·24 cc. of the H_2SO_4 solution. There remained in hand the identical solution of H_2SO_4 originally used, and this was diluted and boiled. A stock solution of As_2O_5 was made from the originally used As_2O_3 by oxidation with HNO_3 (Menzies and McCarthy, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2021). Since HI could only be introduced in the form of KI, a corresponding reduction of 1·2 grms. borax and an increase of 0·78 grms. H_3BO_3 is called for in the buffer. The various buffer solutions necessary were made from single bottles of the chemicals. Various mixtures of the above ingredients were titrated with N/200 I and starch in a total volume of 200 cc. to the first appearance of a plain and persistent colour, whatever the tint might be. The titrations were made by allowing the I solution to drop constantly from a burette at the rate of 1 drop in three seconds, the drops actually entering the titration being caught at half-minute intervals. Frequent tests showed that 1 cc. was very consistently delivered in 32 drops. The following table gives the results obtained:—

Run No.	KI. Grms.	H_3BO_3 Grms.	$Na_2B_4O_7.10H_2O$. Grms.	H_2SO_4 sol. Grms.	Oxidised As_2O_3. Grm.	N/200 I. Drop.
1.	1	0	0	0	0	2—3
2.	4	0	0	0	0	3
3.	4	5	0	0	0	2—3
4.	4	5	10	0	0	5—6
5.	4	5	8	0	0	5—6
6.	4	6	8	0	0	5
7.	4	6	8	7	0	4
8.	4	6	8	7	0·4	4—5

It will be noted that, although the mixtures were made up slightly to exaggerate possible effects, the original blank, represented by Run 4, falls behind the true blank, Run 8, by at most 2 drops N/200 I. Next, to a mixture prepared as in Run 8 was added 13 drops (0·406 cc.) of N/200 I, and a mixture prepared as in Run 4 was titrated by the drop method at half-minute intervals until the colours matched. Triplicate comparisons showed between 16 and 17 drops to be necessary, and no difference between the final tints could be detected. Therefore the original blank falls behind the true blank by at most 4 drops N/200 I, or 0·125 cc. This quantity represents 0·00008 grm. I or a maximum error of 1 part in 10,000, which may possibly have occurred in the blank as originally obtained.

GREEK EXHIBITION.

As stated in the attached speech, the Exhibition in Athens of British Manufactures had its origin in a suggestion made last October by the important delegation of Greek business men who toured industrial England under the auspices of the Federation of British Industries. Having investigated, through a Special Commissioner, the extraordinary scarcity of every kind of manufactured article in Greece and the neighbouring Balkan and Levantine countries, the Federation agreed with Greek opinion that an Exhibition would offer very extensive opportunities to British manufacturers. The Exhibition, therefore, is now in active process of organisation.

The Greek Government, as part of its support of the idea, has lent for the purpose of the Exhibition the "Zappeion" building, close to the Royal Palace and the centre of the town, and specially and admirably constructed for Exhibition purposes. Although applications for space have been received only during the last three weeks or thereabouts, already a third or more of the available space has been taken up. Nearly all the most important branches of British manufacture are already represented.

In addition to the "Zappeion," the Greek Government has granted the use of an extensive piece of land on which

an "Extension" is being erected. This will house such of the larger exhibits as cannot conveniently be placed in the "Zappeion," and it will afford an admirable practical exposition of such articles as agricultural machinery, since land and space are available on which they can be shown actually at work.

As is well-known, the policy of M. Venizelos, and of the strong majority he represents, is to develop both the existing agriculture of Greece and the manufacturing industries she does not yet, but ought to, possess. In view of this, of course, the Machinery Section of the Exhibition will be of very great importance. The Exhibition will, however, appeal to a very much larger field than Greece alone. The trade of Asia Minor, Turkey, and, to a great extent, the Balkan countries, is almost entirely in the hands of Greece. Special arrangements are being made to interest these distant traders and to bring them to the Exhibition. Thence they will carry back with them their impressions of British products, and, most important of all, they will have had an opportunity of coming into contact with the representatives of firms in the Exhibition, and of forming a firm foundation for future business.

Major Kennard, the Federation's Commissioner to Greece, who is shortly to be established permanently in Athens, has been touring all the principal industrial centres of England giving manufacturers the benefit of his experience. The interest he has excited has been very great. In many cases manufacturers have been astonished by the information he was able to give them regarding present trade conditions and opportunities in the near East—opportunities to which other nations are already very keenly alive, as is shown by the efforts they are at present making to establish themselves in the Levantine market. The accompanying notes are a condensed version of the address Major Kennard has been giving.

Extracts from Lecture by Major E. Kennard.

You will probably all of you remember the visit of the Greek Commercial Delegates to this country last autumn, and I think it was the interest aroused by that visit that first gave birth to the idea of having a commercial representative of the Federation in Greece. It was also the members of the Greek Mission who suggested an exhibition of British industries to be held in the "Zappeion" Building in Athens.

The day after my arrival in Athens I visited the "Zappeion," and although, from the descriptions given to me by the members of the Greek Mission, I was prepared for something rather special in the way of buildings, I must confess that the actual sight of it almost took my breath away. It stands in the very best part of the town, at the top of a gentle slope, within a few minutes walk of all the leading hotels, and close to the tramlines. From the steps you see the Acropolis, close to you, on your right; on the left is the Stadium, seating 40,000 people, and constructed entirely of white marble (of which most of you have no doubt seen illustrations), whilst, in the foreground, is a large open gravel space, and beyond that again gardens full of palm trees, orange trees, &c., with a delightful glimpse of the sea in the far distance.

His Majesty's Minister, Lord Granville, from the moment of my arrival, took the deepest interest in the plans of the Federation, both as regards the Exhibition and the extension of British trade in Greece and the Near East generally, and throughout my stay rendered me every assistance in his power.

During the two months I was in Greece, I talked with people of all classes, chiefly commercial, both English and Greek, and never did I hear any other opinion except that the idea of holding an Exhibition of British Industries in Athens as soon as possible after the conclusion of Peace was the very best possible means of forwarding the interests of British commerce in the Near East. I say "Near East" advisedly, for though, at the moment, we are concentrating on Greece, and there is no doubt an immense volume of remunerative trade to be done there, you should remember that Greece only forms a small portion of the Balkans and Levant.

With regard to noting the outlets for British produce in Greece, I would particularly urge upon your attention that owing to the fact that Peace has not been actually signed, Greece is at the moment the only country in that part of the world which is readily approachable from a commercial standpoint, but you should look upon Greece merely as a stepping-stone (an important one, I admit) to the trade of the whole of the Balkans and Levant. Fifty or sixty years ago Great Britain had practically a monopoly of that trade, but, from various causes, this was gradually wrested from us and secured by Germany and Austria; not only secured, but very largely increased. Before the outbreak of war it looked as though this trade was lost to us for ever, but owing to the events of the last four years Germany and Austria have been temporarily (I say advisedly "temporarily") knocked out, and we have now an opportunity which I think you will agree with me, we are unlikely ever to have again. The Greek nation is at present extremely Anglophile, and you must remember that there is a very large Greek element spread throughout the Balkans and Levant which, once we have secured our proper share of the trade of Greece herself, should be of the utmost assistance to us in obtaining a similar share of the trade of those other countries. At this moment it might almost be said to be ours for the asking. I don't think I exaggerate when I say that the Greeks would rather buy British goods than any other. They would rather trade with us than with any other nation, but they are at the moment absolutely denuded of every kind of commodity, from boot-laces to locomotives, and they *must* be supplied immediately, from *some* source. I can give you a small incident which will bring home to you the absolute lack of the most ordinary necessities of life at present prevailing in Greece. During my stay there I had a rather severe attack of influenza, and the medicine that was supplied to me by the leading chemist of Athens arrived in a ginger-beer bottle, stopped with a piece of newspaper. That other nations are bidding strongly for the trade of the Near East is proved by many facts, amongst others I may tell you that the American Consul-General for Greece applied for three Vice-Consuls during my stay in Athens. At the moment I maintain that we hold a distinct advantage over other competition. I am sure I am right in saying that if Greece at this moment were in a position to select one nation from amongst the nations of the world, to whom she would give the whole of her trade, that nation would undoubtedly be Great Britain, but you must remember that Greece is not in that position. Anglophile though she may be she has to live. Naturally she will try to obtain the best goods in the cheapest market. Not only will she try to obtain them, but in the unfortunate position in which she now is, she *must* obtain them *at once*. Greece believes, and I firmly believe that she is right in this belief, that the best of everything, from fighting men to metal-ware, is to be found in Great Britain. She has this belief at the moment, but it will not last for ever. Other nations are leaving no stone unturned to prove to her that they can fill her needs as well as we can. Not only that, but some of them advance the tempting argument that they are in a better position to give to her immediate delivery than we are. I therefore venture again to suggest to you the advisability of taking the long view, and of supplying immediately those commodities of which she is in such dire need.

I have had the honour—my use of the word "honour" is no *façon de parler*—of meeting M. Venizelos and many of his Ministers, and I am in a position to state that it is the intention of the Greek Government to develop Greece in all directions, Political, Agricultural, Mineral, and so forth. I know for a fact that the present Government has already taken steps in this direction, and I know something of their plans for the future.

This war has seen the connection by rail of the ports

Piræus and Salonica for military purposes, and I have reason to believe that this railway is to be developed for commercial purposes. Think what this means—a trunk line throughout the length of the land, with a statesman at the head of affairs who is passionately devoted to, and a firm believer in, the future welfare of this country. Greece is full of undeveloped mineral wealth, and from this trunk line will radiate branch lines, giving, in themselves, opportunities to British manufacturers. Further than that, you are aware that in any country, developed or undeveloped, the arrival of a railway means an increase in the population and industries of the regions through which that line passes, and this means yet more outlets for British produce—outlets which in the near future you will be so anxiously looking for in vain if you do not seize present opportunities.

At the commencement of my remarks I told you that one of the first objects for which I was sent out to Greece was to inspect, and if I thought fit, to secure the use of, the "Zappeion" Building for our Exhibition of British Industries. I took the precaution of sending commercial men, both English and Greek, on the spot, as to the advisability of holding the Exhibition, for I foresaw that if the Exhibition was organised, advertised, and proved a failure, it would lead to great disappointments both in Greece and at home.

I would point out to you that the Exhibition which we propose to hold will be in its way unique. Big Exhibitions of various kinds have been an almost common annual event in all parts of the world in pre-war days, but I think I am right in saying that this Exhibition of British Industries will be extremely practical. It will be a purely *selling* Exhibition. I venture to assert that every exhibitor who can guarantee immediate, or at all events quick delivery of bulk to the samples which he exhibits, will not only pay his expenses but will make a very large and immediate profit, without undue expense or risk. Further than that, he will have the comfortable feeling that he is doing his bit for his country in the great economic war upon which we are now embarked.

We will hold this Exhibition on such a scale that it will attract all classes of buyers, not only from Greece but from many or all of the Balkan States and the Levant. As I said before, all these countries need everything, and need it at once.

The Greeks have plenty of money, and—born traders that they are—they are longing to turn it over, and they *want* British goods. Are you going to supply them? I should like to see British products in every shop and every home in the Near East. It is up to you manufacturers to bring about this very desirable state of affairs. To show you that the Greeks themselves have a similar feeling, I may tell you that I brought with me from Greece an offer from a Greek gentleman to put up the sum of £40,000 towards the erection of a depot for purely British goods in Athens, on the understanding that it would be organised and run by Englishmen.

Remember that in arranging this Exhibition the Federation has no axe of its own to grind; its one and only object is to promote the interests of its members, and, through them, the interests of British Industries as a whole.

I have taken up a most unconscionable amount of your valuable time, for which I humbly apologise. The excuse I offer is that I have been on the spot, I have studied the conditions, and although I frankly confess that I started as a pessimist, I equally frankly confess that I have returned to this country a real optimist as to the possibilities for British trade in the Near East, using Greece and our Exhibition as a stepping stone.

Institution of Electrical Engineers.—At the meeting on April 24, at the Institution of Civil Engineers, Great George Street, Westminster, at 6 p.m., Major A. C. Fuller, R.E., will read a paper on "The Fullerphone and its application to Military and Civil Telegraphy."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 3, 1919.

Sir J. J. Thomson, O.M., President, in the Chair.

The following papers were read:—

"*Note on the Intensity Decrement in the Balmer Series.*" By T. R. Merton, D.Sc., and Prof. J. W. Nicholson, F.R.S.

Twelve members of the Balmer series of hydrogen have been observed in vacuum tubes containing a trace of hydrogen in helium at a pressure of 41 mm. of mercury. In contrast with the diffuse appearance of the last of these members in pure hydrogen, they were observed in the present instance as sharp though faint lines.

A quantitative comparison of the intensity distribution in these tubes containing pure hydrogen, water-vapour, and a mixture of hydrogen and helium at low pressure, has shown that the visibility of the higher members of the series in the high pressure tubes is most probably due to the fact that the energy under these conditions is concentrated within narrow limits of wave-length, instead of being distributed through a broadened line whose energy content is, in fact, greater.

The observed results seem to be incompatible with the quantum theory of the hydrogen spectrum developed by Bohr.

"*Determination of the Secular Accelerations of the Moon's Longitude from Modern Observations.*" By Prof. E. W. Brown, F.R.S.

"*Inter-crystalline Fracture of Metals under Prolonged Application of Stress.*" By W. Rosenhain, D.Sc., F.R.S., and S. L. Archbutt.

The authors' observations have shown that in a number of metals, including lead, mild steel, and an alloy of aluminium with zinc and copper, the prolonged application of stress will, in certain cases, produce an abnormal type of fracture in which the crystals become separated from one another, instead of being broken or torn across in the normal manner. An exact similarity to this type of fracture is found in the "season cracking" of brass. In the latter case the applied stress is an internal one arising from elastic deformation. The authors base an explanation of this type of fracture on the hypothesis, formerly advanced by one of them and widely accepted among metallurgists, that the constituent crystals of metals are held together by thin layers of an amorphous inter-crystalline "cement," whose properties resemble those of a greatly under-cooled liquid. When stresses are applied to such an aggregate, the viscous under-cooled liquid films behave, in the first instance, like a very strong and hard material (somewhat resembling glass), and when fracture is brought about at any ordinary rate it occurs by the failure of the crystals themselves and not by the tearing away of one crystal from another. Under the prolonged action of stress, however, the viscous cement will, in favourable circumstances, yield slowly, so that the crystals become detached from one another. Whether this will occur or not must depend upon the character of the inter-crystalline boundaries; if these are rough and irregular, viscous flow will be prevented, but if they are very smooth it will be facilitated. The authors' observations show that in the cases where inter-crystalline failure occurs the metal has been subjected to some annealing process which has allowed the crystals to acquire smooth regular boundaries; where such smooth boundaries do not exist this type of failure is not met with. The practical importance of avoiding such "over-annealing" is pointed out. As the viscosity of a liquid rapidly decreases with rising temperature, it would follow that inter-crystalline failure of this

type will be favoured by a slight rise of temperature; this is known to be the case with brass, and the authors point out that cases of inter-crystalline cracking in steel have mainly been met with in the plates of steam boilers working at high temperatures.

"*Zonal Harmonics of High Order in Terms of Bessel Functions.*" By J. R. Airey, D.Sc.

A formula expressing the zonal harmonic $P_n(\theta)$ in terms of the Bessel functions $J_0(z)$ and $J_1(z)$ has been given by Lord Rayleigh, viz.,—

$$P_n(\theta) = J_0(z) + \frac{1}{12a^2}\{z^2 J_0(z) - 2z J_1(z)\},$$

where $z = a\theta$ and $a^2 = n(n+1)$, which is specially applicable when n is large and θ is small. Further terms in the coefficients of J_0 and J_1 have been found, requiring the evaluation of integrals involving Bessel functions:—

$$\int x^{2n} J_0 J_1 dx \text{ and } \int \frac{x^{2n+1} J_1^2}{J_0^2} dx + 2n \int \frac{x^{2n} J_1}{J_0} dx.$$

In its extended form:—

$$P_n(\theta) = \left(\alpha + \frac{\beta}{a^2} + \frac{\gamma}{a^4} + \dots\right) J_0(z) - \left(\alpha^1 + \frac{\beta^1}{a^2} + \frac{\gamma^1}{a^4} + \dots\right) \frac{\theta}{6a} J_1(z).$$

Tables of the coefficients, α, β, γ, &c., which are functions of θ only, have been calculated to give the values of $P_n(\theta)$ to six decimal places for each angle of the quadrant. The formula can be employed even when the order n of the function is comparatively small and the argument θ as great as $\frac{1}{2}\pi$.

NOTICES OF BOOKS

A Manual of Chemistry. By Arthur P. Luff, M.D., B.Sc., F.R.C.P.Lond., F.I.C., and Hugh C. H. Candy, B.A., B.Sc.Lond., F.I.C. Sixth Edition, enlarged. London, New York, Toronto, and Melbourne: Cassell and Company, Ltd. 1918. Pp. xix.+745. Price 12s. net.

There can be no doubt that the medical student derives great advantage from the use of a book on chemistry which has been specially written to meet his requirements, and of such works this is one of the very best and most appreciated, as may be gathered from the number of editions through which it has passed. All the chemistry, inorganic and organic, theoretical and practical, which the student requires for the First Professional and First and Second M.B. Examinations is included, and it will be a great convenience to have it all brought together in one volume, which although much enlarged is still quite moderate in size. A sound general knowledge of the elements of chemistry could be obtained from the book, and the authors have taken special care to give the student an insight into fundamental principles while keeping well in view his particular requirements. In the sixth edition much more organic chemistry has had to be included than heretofore, and the sections on the sugars, cyanogen, urea, uric acid, and amino acids have been considerably extended. More practical work is also described, and all that prescribed for the First Professional snd First and Second (Part 1.) M.B. Exaaminations is fully covered.

BOOKS RECEIVED.

"Van Nostrand's Chemical Annual." A Handbook of Useful Data for Analytical, Manufacturing, and Investigating Chemists, Chemical Engineers, and Students. Fourth Issue, 1918. Thoroughly Revised and Enlarged. Edited by John C. Olsen, A.M., Ph.D. Pp. xiii+778. London: Constable and Co., 10, Orange Street, Leicester Square, W.C. 15s. net.

NOTES.

The funeral of Sir William Crookes took place on Thursday last, April 10. A service at St. John's Church, Notting Hill, was conducted by the Rev. H. Mackean. The chief mourners were Mr. and Mrs. Bernard Crookes, Mr. Walter S. Crookes, Mr. and Mrs. L. P. Crookes, Mr. and Mrs. A. J. Cowland, Mrs. Henry Crookes, Mr. Charles Crookes, and the grandchildren, Miss Enid, daughter of the late Joseph Crookes, and Master Willie Crookes, the son of Mr. L. P. Crookes. The congregation included representatives of all the learned Societies in London, personal friends of Sir William. Among those present were Sir Joseph Thomson, O.M. (Master of Trinity College, Cambridge, representing the Royal Society), the Hon. R. Clere Parsons (representing the Royal Institution of Great Britain), Sir Boverton Redwood (representing the British Science Guild), Prof. John Perry (representing the Briitsh Association), Sir Herbert Jackson (President of and representing the Institute of Chemistry), Mr. W. M. Mordey (representing the Institute of Electrical Engineers), Sir William Tilden, Sir Lawrence Jones (representing the Society of Psychical Research), Prof. Frank Clowes, D.Sc. (past President of and representing the Society of Chemical Industry), Dr. Alex. Scott (Vice-president of and representing the Chemical Society), Mr. W. F. Reid (chairman of the Institute of Inventors), Sir David Prain, Sir J. Larmor, M.P., Sir William Davison (Mayor of Kensington), Dr. Abraham Wallace, Dr. Francis Fox, Lady and Miss Macdonell, Dr. Donald Hood, Dr. Emerson Reynolds, Dr. and Mrs. Henry Armstrong, Sir John Snell, Prof. A. Schuster, and a number of representatives of the Notting-hill Electric Lighting Company. After the service at the church the members of the family proceeded to the Brompton Cemetery, where a further short service was held, and the body of Sir William was deposited in the family grave beside that of Lady Crookes, who died in May, 1916.

The British Science Guild has decided to organise an Exhibition in July and August on the lines of those held last year in London and Manchester. This year's exhibition will be on a much larger scale and will be held at the Central Hall, Westminster. The objects of the Exhibition are to illustrate recent progress in British Science and Invention and to help the establishment and development of new British industries, and will deal with the following subjects:—Agriculture, Aircraft, Chemistry, Education, Electrical Apparatus, Engineering Fuels, Medicine and Surgery, Metallurgy, Paper—Illustration and Typography, Physics, and Textiles. Each Section will be under the management of a Committee. Chemistry will receive special attention. The committee appointed for this section is as follows:—Walter F. Reid (Chairman); E. F. Armstrong, D.Sc.; J. C. Cain, D.Sc.; J. H. Gardiner; C. A. Keane, D.Sc.; Robert Mond; Prof. J. C. Philip, D.Sc. The Exhibition will enable new machines, appliances, and devices to be displayed before a large public. It will thus provide inventors with an opportunity of demonstrating the products of their ingenuity, and progressive manufacturers with a place to show the uses they have made of science and invention in new, or the development of old, industries. It is intended to publish a descriptive catalogue of exhibits similar to that issued last year and containing articles upon matters relating to scientific and industrial research of interest to manufacturers. Arrangements are also being made for the delivery of lectures upon important lines of progress, and several conferences will be held with the view of promoting exchange of views between makers and users, and scientific workers and industrialists. Demonstrations and the exhibition of kinematograph films of scientific and technical interest will be given daily, and as many as possible of the machines and accessories will be shown in action.

Mr. GEORGE HUBBARD, F.S.A., F.R.I.B.A., speaking at the Royal Institute of British Architects on February 3, on the Construction of a Dew-pond, described how it was possible to obtain a water supply in the absence of springs, rivers, and rain. At the outset he explained that the atmosphere which was warmed during the day was capable of containing a greater percentage of aqueous vapour than it could retain if it were chilled below the dewpoint during the night. The deposition of the aqueous vapour took place freely upon a condensing surface thermally isolated from the earth by a good non-conductor of heat. He referred to the ancient dew-ponds which formed the water supply to Neolithic man in his settlements on the hill tops, and to natural dew-ponds in the Colesberg district of Cape Colony, where, in the absence of springs, streams, and rains, ponds have a higher water level in the morning than they had in the previous evening. Mr. Hubbard proceeded to explain how he and his brother constructed a dew-pond in a very low-lying piece of land to test the question as to whether it would be possible to obtain a water supply even under unfavourable conditions in the absence of rain, springs, or streams. They began by excavating the earth over an area of 100 ft. square to a depth of 1 ft. 6 in.; over this they laid a bed of 4 in. of cement concrete and thickly coated the surface of this with pitch. The surface of the pitch was then spread over with fine sand, and mica slabs 2 ft. square and 2 in. thick were laid in regular order on top of the sand; about an inch space was left around each slab. In order to keep these slabs quite dry and so preserve their heat non-conducting property, the whole surface of the pond was covered with ⅝ in. of asphalt. The asphalt ran into spaces between the slabs, but when it was completed it represented an even black appearance over the whole pond. At an early hour on an autumn morning, after a rainless night, the pond presented an extraordinary appearance. The whole surface looked like a chess-board with some 2500 perfect white squares all ruled off regularly by hard pitchblack lines about 1 in. wide between them. There was very little dew on the grass around the pond, but in the pond, immediately above each mica square, tall white hoar frost was standing, but there was not a trace of hoar frost on the asphalt above the joints, which stood out as hard black lines. In a few hours the sun melted the hoar frost, and hundreds, if not thousands, of gallons of water lay in great pools and puddles on the surface of the pond. It was a comparatively warm day, and the asphalt, protected as it was by the mica slabs, retained the heat, and the sun in the course of the day dried up the pond.

A VERY simple method of estimation of the quantity of dew deposited naturally on grass is described in the *Meteorologische Zeitschrift*, xxxv., 48, by Dr. V. Parchinger, who places a sheet of blotting-paper on the grass to absorb the dew and subsequently determines its increase of weight. The highest value mentioned for the dew-fall is 0·17 mm.

DIAMONDS are, in value, far and away the most important product of South-West Africa, though the best deposits in which they are found are rapidly being worked out. The gravel which contains them lies in a strip along the coast, and no stones have been discovered more than fifteen miles from the sea. The deposits were first made known in April, 1908, and were so actively exploited during subsequent years that in 1913 they yielded over 20 per cent in value of the total diamond output of the world. The yield for that year was 1,284,727 carats, valued at £2,698,500. During 1914 the production of 1913 was left far behind. Up to August, 1914, 5,400,000 carats had been recovered, valued at nine and a quarter millions sterling. The average size of the stones increases steadily from north to south until it reaches a maximum in the Pomona area. The diamonds are quite unlike those washed from the blue ground of Kimberley or the Transvaal. In hardness and brilliancy they resemble Brazilian stones, and though small in size show a quality uniformly good. The largest stone discovered by the Germans was 34½ carats; the average size varies from a fifth to a sixth of a carat. The layers of diamond-bearing gravel are usually from 4 to 6 inches thick, but between Luderitz Bay and Elizabeth Bay they sometimes extend to 25 and even 30 feet. In the rich holdings of Ida Tal, Pomona district, the gravel has yielded 200 carats per cubic metre at a working cost of 2s. 2d. per carat. In the poorer and more distant workings the cost has run up to 35s. a carat. Before the war the diamond industry employed some 500 whites and 5000 coloured labourers (Cape Boys and Ovambos). The richest and most accessible deposits have already been worked out, and although the recovery of diamonds is considered likely to continue for some time to come, the "life" of the fields was not expected by the Germans to extend beyond twelve or fifteen years. No important new areas have been discovered since 1910, though prospecting has been vigorously pursued. The German Government of the Protectorate controlled the sale of diamonds through the Diamenten-Régie, formed in 1900, and in 1914 definite quota was assigned to the individual mining companies. The purpose was to keep the market steady, to maintain profits, and to encourage development. The profits made by companies which secured rich holdings were almost beyond belief. The Koloniale Bergban-Gesellschaft during the four years 1910 to 1913 distributed dividends amounting in the aggregate to 112 times its capital of £5025. These dividends, of which the highest was 3800 per cent for 1912, were distributed after meeting the heavy Government taxes.—*Board of Trade Journal.*

GERMAN trading interests are already making arrangements for the importation into the United States of German and Austrian china and earthenware. According to information from an authoritative source, interviews have taken place in New York to arrange for the handling of these goods. Their view is that there will be a considerable market for them here if they can be bought at a cheaper price than English, Japanese, or domestic goods. It is reported that one German agent has already made plans to obtain a large quantity of china, and that the goods will be marked "Made in Bohemia" or "Made in Bavaria," as it is believed that the buying public can easily be persuaded that neither of those countries was responsible for German aggression.—*Board of Trade Journal.*

DURING the war the manufacture of paper underwear received special attention in Germany, and it is reported that very considerable advance was made. Paper garments are said to have been produced that were soft to the touch and could be washed repeatedly without deterioration.

WE are glad to announce that Messrs. Ilford, Ltd., the well-known photographic plate makers, have been able to greatly reduce the prices of their plates, and that they are no longer asking for the return of old negative glasses.

S. AND A. GALBRAITH, Manufacturers and Merchants, Kyle Factory, Cumnock, desire to get into touch with publications dealings with preserve and sugar-boiling trades.

NOTES FROM FOREIGN SOURCES

Chlorine Index as a Comparative Measure of the Richness of Soils in Humus.—L. Lapicque and E. Barbé.—The authors have shown that when sodium hypochlorite (Eau de Javel) acts on arable soils it loses active chlorine in proportions which vary within very wide limits. This effect is a measure of the amount of humus in the soil, and a method of classifying soils in the order of their richness in humus may be based upon it. This method, of which the details are given, has the advantage

of being very rapid, and the process can be carried out on the spot.—*Comptes Rendus*, clxviii., No. 2.

Method of Rapid Reduction of Potassium Chloroplatinate.—M. Horsch.—In all methods of determining potassium by the reduction of potassium chloroplatinate the platinum is weighed in the form of powder, and has to be washed, filtered, dried, and ignited with the filter, which involves waste of time and probable loss of material. The new method described by the author is very rapid and simple, and gives satisfactory results. The salt is dissolved in boiling water, alcohol is added, and the solution is evaporated to dryness in a platinum crucible over a water-bath. The metallic platinum then forms a coherent and uniform film on the walls of the crucible. Formaldehyde effects the same reduction, but the film does not adhere completely and the process is less rapid. —*Comptes Rendus*, clxviii., No. 3.

Constitution of Nitrous Fumes.—P. Jolibois and A. Sanfourche.—If air and nitric oxide are mixed in the proportions necessary to make N_2O_3 combination is instantaneous; at the end of one-tenth second the reaction is complete. After 100 seconds contact no nitric compounds are formed, showing that gaseous N_2O_3 is not dissociated in these conditions. If air and nitric oxide are mixed in the proportions necessary to form NO_2 the N_2O_3 stage is very rapidly reached. After one second no appreciable amount of NO_2 is formed, while after 100 seconds the transformation is almost totally effected.—*Comptes Rendus*, clxviii. No. 4.

α- and β-Oxydihydrocinchonines and their Rôle in the Production of Certain Isomers of Cinchonine.—E. Léger.—The author has previously shown that α-oxycinchonine is really an oxydihydrocinchonine, resulting from the fixation of H_2O at the double bond of cinchonine. To find out whether the β isomer has the same origin he has studied the action of HBr and H_2SO_4 on it. Like the α derivative the so-called β-oxycinchonine did not yield a hydrobromo derivative containing an O more than cinchonine, but hydrobromocinchonine and hydrobromo apocinchonine. These two compounds were accompanied by isomers of cinchonine—cinchonigine, cinchoniline, apocinchonine, δ-cinchonine, and some unaltered β-oxycinchonine. When 50 per cent H_2SO_4 acts on the β isomer cinchoniline is the chief product, mixed with cinchonigine, and the same compounds are obtained with 70 per cent acid, the yields being increased. Thus the so-called β-oxycinchonine is really an addition product of H_2O and cinchonine. The α and β compounds are stereo isomers, and their rotatory powers differ only slightly.—*Comptes Rendus*, 1919, clxviii., 404.

Constitution of Geraniol, Linalool, and Nerol.—M. Verley.—The author believes that geraniol, which is easily obtained by reduction of citral, possesses the formula—

$$CH_3{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_2{-}OH$$

and corresponds to citronellol. Two distinct isomeric forms exist of the substances of the geranic series which are found in nature, *i.e.*, geraniol, citral, linalool, and methylheptenone. The α form is much the most abundant; it is often accompanied by the β modification, but the latter occurs in small quantities only. Only very small amounts of nerol occur. Nerol or β citral accompanies citral in essence of lemongrass, and isolinalool is similarly associated with ordinary linalool. Dipentene is easily obtained directly from geraniol by loss of water and closing of the chain, a reaction which is readily brought about by the action of certain dehydrating agents such as formic acid. As geraniol is the oxygen derivative which is most widely distributed in natural essences, where limonene also occurs in great abundance, it is possible that these two compounds are derived from one another. The terpene which corresponds to nerol is the terpinolene which is the β modification of the dipentene—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C=C<\!\begin{matrix}CH_2-CH_2\\CH_2-CH\end{matrix}\!\begin{matrix}\searrow\\ \nearrow\!\!\!\nearrow\end{matrix}\!C-CH_3.$$

Like nerol this terpene is rare. It is spontaneously transformed into dipentene in the cold, and rapidly when warmed to 230° in presence of water.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 68.

Researches on Molecular Transpositions of α-Glycols.—A. Orékhoff.—According to Werner's theory of valency the attractive force of an atom of carbon does not represent four distinct forces, pre-existent and oriented in space, but is a single force acting in all directions from the centre of the atom. Valency is only an empirical relation according to which atoms unite with one another; the total affinity of an atom may be regarded as constant, while the force of combination of the carbon atom with other atoms may vary within wide limits. This theory provides satisfactory explanations of the molecular transpositions of α glycols. Different radicals possess different "aptitude for migration" or "relative mobility." The nature of the migrating radical may be modified by the introduction of substituting radicals in the benzene nuclei. The nature of the dehydrating agent may have a considerable influence on the orientation of the transposition. The group $C_6H_5CH_2$ possesses a mobility and a saturation capacity less than the group C_6H_5.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 9.

Action of Alcoholic Iodides on Neutral Sodium Phosphate in Aqueous Solution.—Octave Bailly.—The alcoholic iodides react on neutral sodium phosphate in aqueous solution, giving, in the case of the first members of the series only, considerable proportions of the corresponding phosphoric mono ether—

$$PO(ONa)_3+RI=PO(ONa)_2OR+NaI.$$

The iodides of methyl, ethyl, allyl, propyl, isopropyl, and isobutyl were used, and deminormal aqueous solutions of trisodium phosphate. The temperature at which the reaction was carried out was 60° in the case of the iodides of methyl and allyl and 100° with the other iodides. The monoether was extracted, after elimination of the unattacked phosphate, in the form of the calcium salt which is very soluble even in the cold. A number of new alkyl phosphates of the alkalis and alkaline earths have thus been prepared. Besides the monoether there is always a small quantity of monophosphoric diether formed—$PO(ONa)_3+2RI=PO(OR)_2ONa+2NaI$. The compounds obtained are really the phosphoric monoethers (alkylphosphates) and not the tautomeric bodies (alkylphosphinates) in which the alcoholic residue would be directly united with the phosphorus. The compounds are hydrolysable with regeneration of phosphoric acid. Generally speaking the solubility of the alkyl phosphates, derived from the monovalent alcohols, of the alkaline earth metals is greatest in the case of the barium salt, less for the strontium, and least for the calcium salt.—*Comptes Rendus*, 1919, clxviii., 560.

New Passage from the Fatty to the Aromatic Series.—I. Komninos.—When malonyl chloride acts on acetone in equimolecular proportions phloroglucine is produced, and at the same time a crystalline substance of formula $Cl.CO.CH_2.CO.CH_2.CO.CH_3$. This substance under the action of calcium carbonate loses HCl and is nearly quantitatively transformed into phloroglucine. The constitutional formula of the latter is justified by this synthesis. This research leads to a new synthetic method, based upon the condensation of the chlorides of acid radicals and ketones, and providing the simplest means of passing synthetically from the fatty to the aromatic series.—*Bull. Soc. Chim. de France*, 1918, xxiii.-xxiv., 449.

Detection and Determination of β-Nitroso-Naphthol.—P. Nicolardot and L. Valli-Douan.—In view of the price of β-nitroso-naphthol it is important to be able to determine it by an accurate method, as commercial products may contain various impurities (unattacked

naphthol, various isomers, &c.). When to an acetone solution of β-nitroso-naphthol a titrated solution of a ferric salt is added, the complex $(C_{10}H_6ONO)_3Fe$, in which the iron is masked, is formed. When all the β-nitroso-naphthol has been converted into complex an excess of ferric salt is revealed by a drop of ammonium sulpho-cyanide. The method can be made rigorously quantitative by adding to the acetone solution of β-nitroso-naphthol an excess of about 10 cc. of titrated ferric salt and 50 cc. of distilled water, shaking for two minutes, and then allowing to stand till the next day. The precipitate then settles, and can be filtered off through a double filter paper. After having been washed it is dried at 70° to constant weight. The molecular weight of β-nitroso-naphthol is 173 and that of the ferric complex is 572. The factor is therefore $\frac{3 \times 173}{572} = 0.907$.—*Bull. Soc. Chim. de France*, 1918, xxiii.-xxiv., 455.

Reduction Products of Oxymethylene Camphor.—H. Rupe, A. Akermann, and H. Takagi.—When oxymethylene is reduced with hydrogen in presence of nickel at the ordinary temperature and pressure, the chief product of the reaction is the keto-alcohol camphyl carbinol. From 80 to 95 per cent of the theoetical amount of this alcohol may be obtained, and 5 to 20 per cent of other substances, the chief of which is methylene camphor. The formation of this compound is due to the abstraction of water by the nickel. The second by-product is methyl camphor, and the ethyl ethers of camphyl carbinol and of oxymethylene camphor are also formed. Although careful search was made there were no traces of a second stereo-isomeric form of camphyl carbinol.—*Helvetica Chimica Acta*, 1918, i., 452.

MISCELLANEOUS.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, after Easter:—Prof. Arthur Keith, four lectures on "British Ethnology—The People of Wales and Ireland." Prof. W. H. Bragg, two lectures on "Listening under Water." Dr. H. S. Hele-Shaw, two lectures on "Clutches." Prof. Frederick Keeble, two lectures on "Intensive Cultivation." Sir Valentine Chirol, two lectures on "The Balkans." Prof. H. S. Foxwell, two lectures on "Chapters in the Psychology of Industry"—(1) "Fourier and other Pioneers in the Movement for the Humanising of Industry"; (2) "Modern Industrial Organization—where it fails to observe the humanities of Industry and the Results." Mr. J. Wells, two lectures (1). "Cæsar's Personal Character as seen in his Commentaries"; (2). "*Cæsar as a General.*" Mr. Julius M. Price, two lectures on "The Italian Front." The Friday Evening Meetings, at 5.30 o'clock, will commence on May 2, when Prof. John W. Nicholson will deliver a Discourse on "Energy Distribution in Spectra." Succeeding Discourses will be given by Sir George Macartney, Dr. S. F. Harmer, Sir Alexander C. Mackenzie, Sir John Rose Bradford, and Prof. Sir Ernest Rutherford.

Relation of Dehydration to Agriculture.—G. C. Prescott (U. S. Dept. of Agriculture, *Circular* 126, January 25, 1919).—Drying has been known for hundreds of years, and is probably the oldest method of food preservation which the human race has employed. In this country it was used in the early colonial days for both animal and vegetable foods. Massachusetts colonists dried corn after it had been cooked, the product being known as samp. Fruits, and especially the apple, were also dried in considerable quantities. Along the coast the drying of fish became an important industry. In other parts of the country other vegetables and fruits and meat products were dried. Peas and sweet corn may be mentioned as examples of the former, while along the Pacific Coast the long sunny period lends itself particularly to the drying of prunes, raisins, and other fruits. In the arid regions of the interior the Indians, and later the early settlers, dried their beef or buffalo meat by cutting into thin strips and hanging up for sun and wind to remove the excess moisture, and sear over the outside with a protective coating which would prevent infection and spoilage. This was known as jerked beef. The advantages of dehydration are almost too obvious to reqûire extended statement. Most evident of all is the loss in weight. Vegetables in common use contain from 60 to 95 per cent of water. The dehydrated product should contain from 5 to 10 per cent of water. There is therefore a very large reduction in weight and consequent saving in transportation charges, which are, in general, based upon weight. Similarly, there is a loss in bulk amounting from 50 to 80 per cent of the bulk of the raw material. From the standpoint of agriculture the greatest advantage of dehydration is in the stabilisation of crops and the conservation of materials. With dehydration the excess of the years of great yield can be stored up and made available in the following year when prices are higher and the crop much smaller. Another great advantage is in the conservation of food materials. It is estimated that over 50 per cent of the fruits and vegetables grown in this country never reach the consumer as a result of poor transportation facilities, irregularities in marketing, of other causes. A third factor of importance in relation of dehydration to agriculture lies in the better diversity of crops that can be secured, and as a result of this the greater variety available to poor and rich alike throughout the year.—*Journal Franklin Institute*, clxxxvii., No. 3.

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PATENTS AND DESIGNS ACTS, 1907-1914.

PHENOL PRODUCTS.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3080.

THE ANALYSIS OF BRASS INGOTS FROM SWARF.

By R. H. DEAKIN, M Sc.

THE following mode of analysis of brass made from swarf has been found accurate and speedy. The elements estimated are Cu, Zn, Pb, Sn, Fe, Al, Ni. The process of analysis is divided into four portions.

I. *Copper* (*varying from* 55 *to* 70 *per cent*)—By the usual iodometric thiosulphate process on 0·50 grm. of the alloy. The addition of 2 cc. 20 per cent sodium phosphate to the acetic solution prevents the iron present from reacting. The true end-point with these brasses is found to be the point at which the colour of the solution changes from reddish-brown (following the purple of starch-iodide) to pale buff, and when a further drop of N/10 sodium thiosulphate produces no further change in the colour of the bulk. Too high results are obtained if the end-point is gauged by the effect of a drop of thiosulphate falling on the surface. Abnormal copper figures are checked by the electrolytic deposition method.

II. *Zinc and Nickel* (*Zinc* 30 *to* 45 *per cent*).—The zinc is estimated by the volumetric ferrocyanide process after removal of the copper as cuprous thiocyanate. 1 grm. of the brass is dissolved in 10 cc. conc. HCl and 2 cc. conc. HNO_3. The HNO_3 is boiled off, and after dilution to 100 cc. the solution is made ammoniacal and then just acid with HCl. Sulphur dioxide is bubbled through the hot solution till the colour pales and 7 cc. 20 per cent ammonium thiocyanate are added. After a further passage of SO_2, and standing for one half hour in a warm place, the CuCNS is filtered off through hard double papers, the precipitate being washed with aired water. (The CuCNS, ignited direct in the gas muffle to Cu_2S with possibly some CuO, serves as a useful check on the volumetric copper).

10 cc. conc. H_2SO_4 are added to the filtrate, and after boiling a few minutes, 5 cc. HNO_3, which completes the destruction of the excess thiocyanate. The solution is then taken to fuming, diluted, lead sulphate filtered off, and to the filtrate 2 grms. NH_4Cl and excess NH_4OH added. From the hot solution the hydrates of Fe and Sn are filtered off and washed well with hot 5 per cent ammonia water containing ammonium chloride.

(Examination of these hydrates shows that with ordinary care not more than 0·03 per cent. zinc is lost at this stage).

The filtrate is boiled to remove excess ammonia, made acid with conc. HCl, and 5 cc. excess added. It is then titrated with a solution of potassium ferrocyanide (1 cc. = approx. 0·01 grm. Zn) after heating to boiling and with a bulk of 250 cc. The external end-point with uranium acetate is soon observed with accuracy once the operator has become familiar with the transient end-point which first appears.

In practice it was found unnecessary to filter off the lead sulphate, since if left in the solution it is partly removed as hydrate with the iron, and moreover what remains has no serious influence on the titration. Zinc foil and zinc oxide were found to contain lead and other impurities, so standardization of the ferrocyanide was finally achieved with pure stick zinc, observing identical conditions of acidity, &c., as with the samples.

Nickel, which is frequently present (trace 0·01, 0·06 per cent), is looked for after removal of the iron and excess ammonia in the above process. It is precipitated as nickel oxime, filtered off, and estimated cyanometrically with N/50 solutions. The zinc solution is boiled down with HCl to destroy excess glyoxime before titrating. Care must be exercised that no zinc hydrate is left on the filter with the nickel oxime.

III. *Lead* (up to 2·0 per cent).—This is estimated by the familiar fuming process with sulphuric acid. The lead sulphate, dissolved in ammonium acetate, being finally precipitated as lead molybdate. With regard to the formation of acid lead molybdates the following is of interest:—

0·1199 grm. of pure lead nitrate (containing the amount of lead present in 5 grms. of a brass with 1·50 per cent. lead) gave—

(*a*). On adding 5 cc. of 5 per cent. ammonium molybdate, all at once, to the boiling ammonium acetate solution of the lead sulphate, a silky yellow precipitate which worked out at 1·57 per lead.

(*b*). On adding the ammonium molybdate drop by drop only (till as far as possible no further precipitate formed), a white granular precipitate, rapid to filter, and which worked out at 1·50 per cent lead. The ammonium molybdate must therefore be added drop by drop.

IV. *Tin* (up to 1 per cent), *Iron* (up to 1 per cent), and *Aluminium*.—The usual method of estimating tin in brasses, by isolation of metastannic acid with HNO_3, leads to contamination of the ignited SnO_2 with iron, if this element is present in the brass.

A method for tin, depending on the quantitative precipitation of the hydrate (Price and Mead, "Technical Analysis of Brass," p. 216) has been tried and, after modification, found satisfactory. It has the advantage of leaving the iron in a reduced condition in solution. 5 grms. of the brass, after careful cleaning with a magnet, are dissolved in 40 cc. of a mixture of 3HCl (conc.), $1HNO_3$ (conc.) After dilution to 200 cc., 2 grms. NH_4Cl and 40 cc. NH_4OH are added. The solution is brought to the boil and filtered through pulp and washed well with hot 5 per cent. ammonia water. The pad is extracted with hot 1 : 1 HCl and cold water back into the same beaker and reprecipitated with ammonia, filtered, and again washed with ammonia water. Then follows a second extraction, this time with cold 1:3 H_2SO_4, which leaves on the pad as sulphate any lead present. 5 cc., conc. H_2SO_4 are added to the extract, which is made up to a bulk of 300 cc., and through it when hot is passed a rapid stream of H_2S. When the solution is saturated it is allowed to stand on the edge of the hot plate till the tin sulphide coagulates and settles. The sulphide is filtered off through hard double pleated papers and washed with H_2S water containing a little sulphuric acid and ammonium acetate. It is then dried, ignited, treated with a little powdered ammonium carbonate, ignited further, and weighed as SnO_2.

Slight contamination with copper and lead occurs and was found by analysis of the ignited SnO_2 from 20 estimations to give an average error of 0·007 per cent Sn (with average 0·3 per cent Sn present). This, however, can be much diminished by exercising greater care in washing out the copper with ammonia water and by using a a substantial pad and cold 1 : 3 H_2SO_4 for the second extraction of the hydrates. The filtrate from the tin sulphide is collected in an Erlenmeyer flask (600 cc.). A filter grate is introduced and the solution is boiled and repeatedly tested with moistened lead acetate paper, held over the mouth of the flask, till no H_2S remains. Thirty minutes boiling is usually sufficient, the bulk after that time being about 250 cc. After rapid cooling, the reduced iron is titrated with N/10 potassium permanganate.

The following figures show that complete reduction, removal of H_2S, and no reoxidation take place. Four portions (0·050 grm.) of iron wire were weighed out. Two were dissolved in 10 per cent H_2SO_4 in Erlenmeyer flasks with Bunsen valves, cooled, and titrated with N/10 approx.

$KMnO_4$. They required 8·40 and 8·45 cc. to oxidise them. The other two were dissolved in HNO_3, and the hydrate, precipitated with ammonia, filtered off and extracted with 50 cc. 1 : 2 cold H_2SO_4. The extract was made up to a bulk of 300 cc., heated to boiling, and H_2S passed for a quarter of an hour. The sulphur was filtered off, 5 conc. H_2SO_4 added, and the H_2S boiled off in 25 minutes. After cooling the solutions were titrated. Both required 8·40 cc. $KMnO_4$.

With known added amounts of tin and iron, together with copper and zinc, as in 5 grms. of a typical brass, the following figures were obtained by this process:—

Sn added Per cent.	Sn found Per cent.	Fe added Per cent.	Fe found Per cent.
0·65	0·64	0·25	0·25
0·27	0·28	0·45	0·45

When it is required to examine the brass for aluminium the filtrate from the tin sulphide is boiled free of H_2S, oxidised with a few cc. of HNO_3 (titration at this stage would introduce manganese, which is best avoided), and the iron and aluminium precipitated as hydrates with ammonia and extracted into excess 30 per cent NaCH with HCl. The iron thrown out is filtered off and estimated as above or gravimetrically. The NaOH solution is made acid with HCl, and the aluminium, after a double precipitation with slight excess ammonia to remove sodium chloride, is ignited to Al_2O_3. Where much tin is present (0·5 per cent or more) a small amount may not be removed as sulphide and will contaminate the Al_2O_3. It can be removed with H_2S before the final precipitation of the aluminium. A blank on the reagents used is essential. Traces only of manganese (0·002 per cent) and bismuth (0·0005 per cent), also arsenic up to 0·03 per cent, are found to occur in these brasses.

MEASUREMENTS OF WAVE-LENGTHS IN THE SPECTRUM OF NEON.

By KEIVIN BURNS, W. F. MEGGERS, and P. W. MERRILL.

THE lines in the neon spectrum are very sharp, a quality which recommends this gas as a standard source wherever the lines have sufficient strength. The ultra-violet group between 3369 A and 3520 A may be used for standards, and there are a few good infra-red lines, but the strength and distribution of the lines in the region 5852A to 7438A make the neon spectrum particularly useful as a comparison in this region.

The wave-lengths of fifty-five lines in the neon spectrum have been measured by means of the interferometer. These lines lie in the region 3369 A to 8495 A. The strong lines in the visible region of the spectrum have been observed with great accuracy, the probable error being one part in several millions, or less than one-tenth the width of the line. These strong lines were observed by means of three different pairs of interferometer plates which were each used on several interferometers. The ultra-violet lines and all the strong lines in the visible were compared directly with the fundamental standard 6438A. Some of the deep red and infra-red lines were compared with well-determined lines in the visible neon spectrum.

One hundred and eighty-nine faint lines in the visible and infra-red neon spectrum have been measured by means of a concave grating. The probable error of these grating measurements is one or two hundredths Angstrom. The region covered by the grating observations extends from 5343A to 8783A.

The constant differences discovered by Watson are found to hold with remarkable exactness in the case of lines which are strong enough to be measured with the highest accuracy. In fact, the differences are exactly constant within the limits set by the accuracy of the wave-lengths.—*Bur. Stands. Sci, Paper No.* 329, 1918, p. 10.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

IN the first lecture an attempt was made, more especially in connection with sulphuric acid manufacture and the production of synthetic ammonia, to demonstrate the value of certain physico-chemical principles as applied to technology. These principles provide a rational basis for the investigation of processes in which questions of chemical equilibrium are involved; they permit a concise formulation of the influence of various important factors, and render possible a real scientific control of such operations when they reach the manufacturing stage.

Exact knowledge, however, of the equilibrium conditions prevailing in such technical gas reactions as those already considered does not suffice for the practical manufacturer. For obvious economic reasons he must raise a question as to the *velocity* of the particular reaction concerned. However favourable the position of equilibrium may be with regard to the desired product, the reaction is of no value from the technical standpoint, unless the attainment of equilibrium is, or can be made, reasonably rapid.

Now the velocity of a chemical reaction, as is well known, can be increased by raising the temperature, but this may involve, as in the instances of the sulphuric acid contact process and the ammonia synthesis, an undesirable shifting of the equilibrium, and consequently a diminished yield of the product. A high yield and rapid completion of the reaction may not both be realisable along these lines.

In addition, however, to rise of temperature there is another recognised method of accelerating a chemical reaction, namely, by the use of "catalysts." These are substances the mere presence of which in contact with the reacting system promotes the change and hastens the establishment of equilibrium. Chemical literature has long recorded observations of a general kind relating to the action of catalysts, but a rational study of their influence and their efficiency can be attempted only on physico chemical lines. In indicating what these lines are it is desirable to recall the way in which the physical chemist arrives at a quantitative expression for the rate of a chemical reaction.

The application of kinetic conceptions to a reversible gaseous reaction, as discussed in the first lecture, leads to the view that progress towards equilibrium, *i.e.*, the net velocity of the change, is determined by the velocities of two opposed component reactions. Thus, if—

$$A+B \rightleftarrows C+D$$

represents the reversible reaction, v_1 the velocity of the change $A+B \rightarrow C+D$, v_2 that of the change $C+D \rightarrow A+B$, and a, b, c, d the concentrations at the moment of the four molecular species involved, then the net velocity of the reaction is given by $V = v_1 - v_2 = k_1ab - k_2cd$. If now it is supposed that the reaction begins with A and B alone present in the concentrations a_0 and b_0, and that after an interval of time t from the start, the concentrations of C and D are both x, the velocity formula becomes $V = k_1(a_0-x)(b_0-x) - k_2x^2$. In the language of the differential calculus $V = \frac{dx}{dt}$, and the progress of this reversible reaction towards equilibrium is therefore represented by the equation—

$$\frac{dx}{dt} = k_1(a_0-x)(b_0-x) - k_2x^2,$$

* Cantor Lecture (II.). Delivered before the Royal Society of Arts, December 9, 1918. From the *Proceedings of the Royal Society of Arts*, lxvii., No. 3451.

where k_1 and k_2 are so-called velocity coefficients, the numerical values of which are a quantitative expression of the rates of the forward and the back reaction respectively.

In cases where the position of equilibrium in the reversible reaction—

$$A+B \rightleftarrows C+D$$

lies practically at the right-hand extreme, the velocity of the back reaction becomes negligible, and the velocity equation may be written $\frac{dx}{dt} = k_1(a_0-x)(b_0-x)$, or simply $\frac{dx}{dt} = k(a_0-x)(b_0-x)$. Integration of this equation leads to the formula—

$$k = \frac{1}{(a_0-b_0)t} \cdot \log_e \frac{b_0(a_0-x)}{a_0(b_0-x)}$$

and if in any particular case the progress of the change can be followed experimentally, *i.e.*, if the values of x corresponding with various values of t can be ascertained, then k can be calculated, and the velocity of reaction at the temperature of experiment is quantitatively expressed thereby. In numerous cases the law of mass action, as embodied in the foregoing expression for k, has been verified experimentally; x, the amount of change in time t, varies with t in such a manner that—

$$\frac{1}{(a_0-b_0)t} \cdot \log_e \frac{b_0(a_0-x)}{a_0(b_0-x)}$$

remains constant.

As an illustration of the extent to which these requirements of the law of mass action are fulfilled in an individual instance the saponification of ethyl acetate by an equivalent amount of sodium hydroxide may be taken. This is a time reaction, the course of which may be followed by extracting samples of the reaction mixture from time to time and titrating for the residual alkali; the quantity of this naturally falls off as the change proceeds. In Table I. the figures for a particular experiment are recorded, those in the first column representing the intervals from the start at which samples were extracted, those in the second column giving the relative alkalinity of each sample (alkalinity of initial mixture = 1·00), and those in the last column giving the calculated values of the velocity coefficient.

TABLE I.—*Saponification of Ethyl Acetate by Sodium Hydroxide.*

Minutes from start.	Relative alkalinity.	Velocity coefficient.
4	0·659	0·129
6	0·570	0·126
8	0·487	0·132
10	0·437	0·129
12	0·388	0·131
15	0·341	0·129
20	0·276	0·131

The satisfactory constancy of the figures in the last column demonstrates the applicability of the law of mass action in this case.

In the reaction—

$$A+B \rightleftarrows C+D,$$

which has been taken as the basis of the argument, two molecules undergo change of concentration as the reaction proceeds, and the velocity coefficient k is accordingly described as the constant for a "bimolecular" reaction. On the same lines as those already followed an expression can be obtained for the velocity coefficient of a "unimolecular" reaction, in which only one kind of molecule undergoes change of concentration; for this case it is found that $k = \frac{1}{t} \cdot \log_e \frac{a}{a-x}$, in which expression a is the initial concentration of the substance undergoing change, and x is its concentration after time t from the start. Where more than two molecules undergo change of concentration, *i.e.*, for reactions of a higher "order" than the second, more complicated expressions are obtained for the velocity coefficient.

With these definite methods for expressing quantitatively the velocity of a chemical reaction at any given temperature, it becomes possible to state the influence of various factors on the velocity by recording the corresponding change in the velocity coefficients. In reference, for example, to the influence of temperature on the rate of a chemical change it is customary to represent this effect by a statement of the increase in k for a temperature interval of 10°; *i.e.*, by recording the value of the ratio $\frac{k_{T+10}}{k_T}$. The study of a very large number of cases has shown that for homogeneous changes, where the reaction system is entirely gaseous or entirely liquid, the value of $\frac{k_{T+10}}{k_T}$ lies, as a rule, between 2 and 3, the velocity being doubled or trebled for a rise of 10° C.

As with temperature so with other factors which affect the rate of chemical change, the velocity coefficient provides a quantitative basis for their assessment. In relation to catalysis, in particular, it becomes possible to state the efficiency of one and the same catalyst at different concentrations, to determine whether the activity of the catalyst remains constant, and to compare the influence of different catalysts under given conditions.

Before proceeding to develop these considerations it is desirable to state definitely what are the characteristics of a catalyst from the physico-chemical point of view. One of the main facts about a catalyst is that its quantity may be, and often is, exceedingly small in comparison with the quantities of the reacting substances which are affected. It has been stated, for example, that in the Schröder-Grillo process for the production of sulphuric acid, in which process the contact mass consists of finely-divided platinum on magnesium sulphate, 5 grms. of platinum are sufficient for an output of one ton of oleum per day, with a loss of only 20 mgrms. platinum. It appears also, to take an example in another field, from information supplied to the writer by Mr. Maxted, that in the synthesis of ammonia with an iron-potash catalyst, an output of something like two tons of ammonia per litre of catalyst space can be obtained before it is necessary to change the catalyst.

Further, in normal circumstances the activity of the catalyst remains unimpaired when the reaction which it has accelerated is at an end. An interesting illustration of this characteristic of catalysts is furnished by Bredig's experiments on the influence of colloidal platinum in promoting the combination of hydrogen and oxygen at ordinary temperatures. In one case 2·5 cubic cm. of colloidal platinum solution (containing 0·17 mgrm. of the metal) were shaken with electrolytic gas, and the decrease in the volume of the gas, due to the combination of hydrogen and oxygen, was determined at ten-minute intervals. Table II. gives the results obtained.

TABLE II.

Time in minutes	Decrease in the gas volume. Cc	Decrease per minute.
10	17·8	1·78
20	35·8	1·80
30	54·8	1·90
40	72·4	1·76
50	90·2	1·78

The figures in the last column of Table II. afford no evidence of any decrease in the activity of the colloidal

platinum as the reaction proceeds. Further, the same colloidal platinum was shaken intermittently for fourteen days with the hydrogen+oxygen mixture, about 10 litres of which were converted to water in this interval. Not only is the contrast between the minute quantity of the catalyst and the extent of the induced change sufficiently striking, but it was found at the end of the fourteen days that the rate of decrease of the gas volume, measured over successive ten-minute intervals with constant shaking, as at the beginning of the experiment, was 2·02, 1·87, 1·95, 1·97, and 2·01 cubic cm. per minute. Plainly, the catalytic efficiency of the platinum is no lower at the end of the experiment than at the commencement.

Now, in the technical applications of catalysis one of the most serious problems has been precisely how to keep the catalyst in a state of unimpaired efficiency. However active the contact substance may be at the start, it is useless from the technical standpoint unless it has a reasonably long life. This difficulty does not arise with a dissolved catalyst, such as an acid in the hydrolysis of starch; but where the catalyst is a solid substance, when we are dealing with a case of so-called "heterogeneous" catalysis, then the problem is a serious one. In many instances the technical development of a promising catalytic reaction has been held up by the difficulty of preserving the catalyst in its full activity. The catalyst deteriorates owing to the presence of some foreign substance, or "poison," in the materials which are reacting under the influence of the catalyst.

A notable example of this difficulty is furnished by the history of the development of the sulphuric acid contact process. So long as absolutely pure gases are employed it appears that the platinum catalyst maintains its efficiency. In one case which has been put on record, where sulphur dioxide, obtained by the evaporation of the liquid substance, was mixed with filtered air and passed over the contact mass a 95 per cent yield of sulphur trioxide was still given by platinised asbestos which had been in the plant for about ten years continuously without renewal. It is a fair inference that the catalytic action of platinum continues indefinitely if pure gases are employed.

The record, however, of the prolonged efforts of the Badische Anilin- und Soda-Fabrik to utilise for the purpose of the sulphuric acid contact process the gases obtained by roasting blende or pyrites demonstrates the extreme sensitiveness of the platinum catalyst to impurities. It was found that even when the pyrites gases were cooled by passage through long metal pipes, repeatedly scrubbed with sulphuric acid, and finally filtered through dry coke and asbestos, the contact mass gradually became less effective, and finally lost its power altogether. The discovery was made that certain substances, notably arsenic, are specially injurious to the catalytic efficiency of platinum, and further investigation showed that even the drastic purification just described had failed to remove the last traces of arsenic from the pyrites gases.

The sulphuric acid "mist" or "fume" in these gases is extraordinarily persistent, and apparently is the carrier of the arsenic. The removal from a stream of gas of those impurities which are in a very finely-divided liquid or solid condition is recognised as sometimes a more difficult operation than the absorption of gaseous impurities by chemical means. In the case of the sulphuric acid contact process it was only after much patient labour that means were found, including slow cooling, thorough scrubbing, and wet filtration, for removing all traces of "poisons" from the pyrites gases. During the last few years a novel method of dealing with all sorts of mist and fume has been introduced by Cottrell, based on the fact that a strong electrical field promotes the settlement and precipitation of suspended particles. Numerous plants involving this principle have been designed and erected, more particularly in connection with smelting works and blast-furnaces, and the same process is being applied for the removal of the mist from the pyrites gases employed in the sulphuric acid manufacture.

The serious difficulties encountered in using pyrites gases in the sulphuric acid contact process gave some support to the belief that the poisoning of the catalyst was inevitable, and it was accordingly suggested that the platinum should be deposited on a soluble carrier, so that when the contact substance lost its efficiency the valuable metal could be recovered quite easily by appropriate treatment. This was the method employed in the Schröder-Grillo process, a very active catalyst being prepared by soaking magnesium sulphate in the solution of a platinum salt, and then heating in the presence of sulphur dioxide; when the contact mass has been formed the platinum is about 0·1 per cent of the whole.

The fact that the amount of a catalyst may be almost infinitely small compared with the quantities of the substances which react under its influence makes it extremely probable that the final state of the reactive system must be independent of the catalyst. This would mean, for a reversible reaction in particular, that the state of equilibrium finally attained will be the same whether the catalyst is there or not. The true catalyst, that is, will influence only the rate at which equilibrium is established, not the position of equilibrium itself, or the energy change accompanying the reaction. The catalyst may be compared to the oil which facilitates the sliding of a weight down an inclined plane, without affecting the total energy derivable from the fall of the weight.

Illustrative confirmation of this important conclusion is furnished by Turbaba's work on the equilibrium between acetaldehyde and paraldehyde. The equilibrium mixture of these two substances at 50·5° contains 33·9 per cent of acetaldehyde and 66·1 per cent of paraldehyde, and the conversion of paraldehyde into this mixture is accompanied by a marked and easily measurable increase of volume. The change is accelerated by a variety of substances, but it was found that with different catalysts in varying quantity the difference in volume of the paraldehyde and the equilibrium mixture is practically the same in every case, as is shown in Table III.

TABLE III.—*Paraldehyde* ⇄ *Acetaldehyde.*

Catalyst.	Per cent. Catalyst.	Percentage increase of volume.
Sulphur dioxide ..	0·08	8·20
Sulphur dioxide ..	0·002	8·19
Zinc sulphate	2·7	8·13
Hydrochloric acid ..	0·13	8·13
Oxalic acid..	0·52	8·27
Phosphoric acid.. ..	0·54	8·10

Clearly, the percentage increase of volume is independent of the particular catalyst employed, and, in the case of sulphur dioxide, independent also of the amount of catalyst. In this case, then, and in fact for all truly catalytic reversible reactions, the catalyst affects only the velocity of the change, not the composition of the equilibrium mixture. If this statement were not correct then the investigation of equilibrium reactions in presence of catalysts and the evaluation of equilibrium constants, as in the sulphuric acid contact process and the ammonia synthesis, would be an unjustifiable proceeding.

If now, in any reversible reaction the position of equilibrium is unaffected by the catalyst it follows that the value of the equilibrium constant K is unaltered. This constant, however, as was shown in the previous lecture, is the ratio of two velocity coefficients, k_1 and k_2, which refer to the forward and the back reactions respectively. It follows therefore that k_1 and k_2 must be affected in an equal degree by the catalyst; that is, the catalyst accelerates the forward and the back reactions in the same proportion. The mere fact that iron and nickel promote the decomposition of ammonia at high temperatures suggested that these metals would act as catalysts for the opposed reaction also, viz., the union of nitrogen and hydrogen. This was found to be the case. Again, in the

absence of a catalyst, sulphur trioxide once formed appears to be remarkably stable at high temperatures, even where the equilibrium constant for the reaction—

$$2SO_3 \rightleftarrows 2SO_2+O_2$$

would require a far-reaching decomposition into sulphur dioxide and oxygen. The rate of decomposition, no less than the rate of synthesis, is determined largely by the presence of an appropiate catalyst.

With these characteristics of catalysts in mind we may endeavour to apply the conceptions of reaction velocity and the formulæ embodying these conceptions for the purpose of a rational study of catalysis. The success which has attended the physical chemist's efforts along these lines has been much more notable in some directions than in others, and it has become clear that a distinction must be drawn between "homogeneous" catalysis on the one hand and "heterogeneous" catalysis on the other. In the former case the catalyst is in the same physical state (gaseous or liquid) as the substances which are reacting; in the latter the catalyst is solid, and cannot be in a condition of true homogeneous mixture with the reacting compounds.

(To be continued).

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

The literature on the colour of water is widely scattered; it appears not to have been read by anybody; and it is somewhat contradictory. It has, therefore, seemed desirable to collect the material in an accessible form as it constitutes an interesting chapter in the general subject of the colours of colloids.

Tyndall ("Fragments of Science: The Sky; Voyage to Algeria; Niagara") has discussed the blue colour of turbid media with special reference to the colour of the sky and of the sea. In Newton's rings the colour nearest to the central black spot is a faint blue—blue of the first order—corresponding to the film of air when thinnest.

"If a solid or liquid, of the thickness requisite to produce this colour, were broken into bits and scattered in the air, Newton inferred that the tiny fragments would display the blue colour. Tantamount to this, he considered, was the action of minute water-particles in the incipient stage of their condensation from aqueous vapour. Such particles suspended in our atmosphere ought, he supposed, to generate the serenest skies. Newton does not appear to have bestowed much thought upon this subject; for to produce the particular blue which he regarded as sky-blue, thin plates with parallel surfaces would be required. The notion that cloud-particles are hollow spheres, or vesicles, is prevalent on the Continent, but it never made any way among the scientific men of England. De Saussure thought that he had actually seen the cloud-vesicles, and Faraday, as I learnt from himself, believed that he had once confirmed the observation of the illustrious Alpine traveller. During my long acquaintance with the atmosphere of the Alps I have often sought for these aqueous bladders, but have never been able to find them. Clausius once published a profound essay on the colours of the sky. The assumption of small water drops, he proved, would lead to optical consequences entirely at variance with facts. For a time, therefore, he closed with the idea of vesicles, and endeavoured to deduce from them the blue of the firmament and the morning and evening red.

"It is not, however, necessary to invoke the blue of the first order to explain the colour of the sky; nor is it necessary to impose upon condensing vapour the difficult, if not impossible, task of forming bladders, when it passes into the liquid condition. Let us examine the subject. Eau-de-Cologne is prepared by dissolving aromatic gums or resin in alcohol. Dropped into water, the scented liquid immediately produces a white cloudiness, due to the precipitation of the substances previously held in solution. The solid particles are, however, comparatively gross; but, by diminishing the quantity of the dissolved gum the precipitate may be made to consist of extremely minute particles. Brücke, for example, dissolved gum-mastic, in certain proportions, in alcohol, and carefully dropping his solution into a beaker of water, kept briskly stirred, he was able to reduce the precipitate to an extremely fine state of division. The particles of mastic can by no means be imagined as forming bladders. Still, against a dark ground—black velvet for example—the water that contains them shows a distinctly blue colour. The bluish colour of many liquids is produced in a similar manner. Thin milk is an example. Blue eyes are also said to be simply turbid media. The rocks over which glaciers pass are finely ground and pulverised by the ice, or the stony emery imbedded in it; and the river which issues from the snout of every glacier is laden with suspended matter. When such glacier water is placed in a tall glass jar, and the heavier particles are permitted to subside, the liquid column, when viewed against a dark background, has a decidedly bluish tinge. The exceptional blueness of the Lake of Geneva, which is fed with glacier water, may be due, in part, to particles small enough to remain suspended long after their larger and heavier companions have sunk to the bottom of the lake.

"We need not, however, resort to water for the production of the colour. We can liberate, in air, particles of a size capable of producing a blue as deep and pure as the azure of the firmament. In fact, artificial skies may be thus generated, which proves their brotherhood with the natural sky by exhibiting all its phenomena. There are certain chemical compounds—aggregates of molecules—the constituent atoms of which are readily shaken asunder by the impact of special waves of light. Probably, if not certainly, the atoms and the waves are so related to each other, as regards vibrating period, that the wave-motion can accumulate until it becomes disruptive. A great number of substances might be mentioned whose vapours, when mixed with air and subjected to the action of a solar or an electric beam, are thus decomposed, the products of decomposition hanging as liquid or solid particles in the beam which generates them. And here I must appeal to the inner vision already spoken of. Remembering the different sizes of the waves of light, it is not difficult to see that our minute particles are larger with respect to some waves than to others. In the case of water, for example, a pebble will intercept and reflect a larger fractional part of a ripple than of a larger wave. We have now to imagine light-undulations of different dimensions, but all exceedingly minute, passing through air laden with extremely small particles. It is plain that such particles, though scattering portions of all the waves, will exert their most conspicuous action upon the smallest ones; and that the colour-sensation answering to the smallest waves—in other words, the colour line—will be predominant in the scattered light. This harmonises perfectly with what we observe in the firmament. The sky is blue, but the blue is not pure. On looking at the sky through a spectroscope, we observe all the colours of the spectrum; blue is merely the predominant colour. By means of our artificial skies we can take, as it were, the firmament in our hands and examine it at our leisure. Like the natural sky, the artificial one shows all the colours of the spectrum, but blue in excess. Mixing very small quantities of vapour with air, and bringing the decomposing luminous beam into action, we produce particles too small to shed any sensible light, but which may, and doubtless do, exert an action on the ultra-violet waves of the spectrum. We can watch these particles, or rather the space they occupy, till they grow to a size able to

* From the *Journal of the Franklin Institute*, clxxxvii., No. 3.

TABLE I.

No.	Location.	Colour of Sea.	Appearance in Luminous Beam.
1.	Gibraltar Harbour	Green	Thick with fine particles.
2.	Two miles from Gibraltar	Clearer green	Thick with very fine particles.
3.	Off Cabreta Point	Bright green	Still thick, but less so.
4.	Off Cabreta Point	Black-indigo	Much less thick, very pure.
5.	Off Tarifa	Undecided	Thicker than No. 4.
6.	Beyond Tarifa	Cobalt blue	Much purer than No. 5.
7.	Twelve miles from Cadiz	Yellow-green	Very thick.
8.	Cadiz Harbour	Yellow-green	Exceedingly thick.
9.	Fourteen miles from Cadiz	Yellow-green	Thick, but less so.
10.	Fourteen miles from Cadiz	Bright green	Much less thick.
11.	Between Capes St. Mary and Vincent ..	Deep indigo	Very little matter, very pure.
12.	Off the Burlings	Strong green	Thick, with fine matter.
13.	Beyond the Burlings	Indigo	Very little matter, pure.
14.	Off Cape Finisterre	Undecided	Less pure.
15.	Bay of Biscay	Black-indigo	Very little matter, very pure.
16.	Bay of Biscay	Indigo	Very fine matter. Iridescent.
17.	Off Ushant..	Dark green	A good deal of matter.
18.	Off St. Catherine	Yellow-green	Exceedingly thick.
19.	Spithead	Green	Exceedingly thick.

eld the firmamental azure. As the particles grow larger ıder the continued action of the light, the azure becomes ss deep; while later on a milkiness, such as we often ›serve in nature, takes the place of the purer blue. inally the particles become large enough to reflect all ıe light-waves, and then the suspended 'actinic cloud' ffuses white light. . . .

"In the harbour of Gibraltar, on the morning of our ›parture, I resumed a series of observations on the colour the sea. On the way out a number of specimens had ›en collected, with a view of subsequent examinations. ut the bottles were claret bottles, of doubtful purity. t Gibraltar, therefore, I purchased fifteen white glass ›ttles, with ground-glass stoppers, and at Cadiz, thanks ı the friendly guidance of Mr. Cameron, I secured a ›zen more. These seven and twenty bottles were filled ith water, taken at different places between Oran and pithead. And here let me express my warmest acknow-*dgments* to Captain Henderson, the commander of I.M.S. *Urgent*, who aided me in my observations in very possible way. Indeed, my thanks are due to all the fficers for their unfailing courtesy and help. The captain laced at my disposal his own coxswain, an intelligent llow named Thorgood, who skilfully attached a cord to ıch bottle, weighted it with lead, cast it into the sea, nd, after three successive rinsings, filled it under my own yes. The contact of jugs, buckets, or other vessels was ıus avoided; and even the necessity of pouring out the 'ater, afterward, through the dirty London air.

"The mode of examination applied to these bottles has een already described. The liquid is illuminated by a owerfully condensed beam, its condition being revealed ırough the light scattered by its suspended particles. Care ı taken to defend the eye from the access of all other light, nd, thus defended, it becomes *an organ of inconceivable* elicacy. Were water of uniform density perfectly free om suspended matter, it would, in my opinion, scatter o light at all. The track of a luminous beam could not e seen in such water. But an amount of impurity so ıfinitesimal as to be scarcely expressible in numbers, and ıe individual particles of which are so small as wholly to lude the microscope, may, when examined by the method lluded to, produce not only sensible, but striking, effects pon the eye.

"The results of the examination of nineteen bottles lled at various places between Gibraltar and Spithead re here tabulated.

"Here we have three specimens of water, described as reen, a clearer green and bright green, taken in Gibraltar larbour, and off Cabreta Point. The home examination ıowed the first to be thick with suspended matter, the ›cond less thick, and the third still less thick. Thus the green brightened as the suspended matter diminished in amount.

"Previous to the fourth observation our excellent navigating lieutenant, Mr. Brown, steered along the coast, thus avoiding the adverse current which sets in, through the Straits, from the Atlantic to the Mediterranean. He was at length forced to cross the boundary of the Atlantic current, which was defined with extraordinary sharpness. On the one side of it the water was a vivid green, on the other a deep blue. Standing at the bow of the ship, a bottle could be filled with blue water, while at the same moment a bottle cast from the stern could be filled with green water. Two bottles were secured, one on each side of this remarkable boundary. In the distance the Atlantic had the hue called ultra-marine; but looked fairly down upon it was of almost inky blackness—black qualified by a trace of indigo.

"What change does the home examination here reveal? In passing the indigo, the water became suddenly augmented in purity, the suspended matter becoming suddenly less. Off Tarifa, the deep indigo disappears, and the sea is undecided in colour. Accompanying this change, we have a rise in the quantity of suspended matter. Beyond Tarifa, we changed to cobalt-blue, the suspended matter falling at the same time in quantity. This water is distinctly purer than the green. We approach Cadiz, and at twenty miles from the city get into yellow-green water; this the London examination shows to be thick with suspended matter. The same is true at Cadiz Harbour, and also of a point fourteen miles from Cadiz in the homeward direction. Here there is a sudden change from yellow-green to a bright emerald-green, and accompanying the change a sudden fall in the quantity of suspended matter. Between Cape St. Mary and Cape St. Vincent the water changes to the deepest indigo, a further diminution of the suspended matter being the concomitant phenomenon.

"We now reach the remarkable group of rocks called the Burlings, and find the water between the shore and the rocks a strong green; the home examination shows it to be thick with fine matter. Fifteen or twenty miles beyond the Burlings we come again into indigo water, from which the suspended matter has in great part disappeared. Off Cape Finisterre, about the place where the *Captain* went down, the water becomes green, and the home examination pronounces it to be thicker. Then we enter the Bay of Biscay, where the indigo resumes its power, and where the home examination shows the greatly augmented purity of the water. A second specimen of water, taken from the Bay of Biscay, held in suspension fine particles of a peculiar kind; the size of them was such as to render the water richly iridescent. It showed itself green, blue, or salmon-coloured, according to the

direction of the line of vision. Finally, we come to our last two bottles, the one taken opposite St. Catherine's lighthouse, in the Isle of Wight, the other at Spithead. The sea at both these places was green, and both specimens, as might be expected, were pronounced by the home examination to be thick with suspended matter.

"Two distinct series of observations are here referred to—the one consisting of direct observations of the colour of the sea, conducted during the voyage from Gibraltar to Portsmouth, the other carried out in the laboratory of the Royal Institution. And here it is to be noted that in the home examination I never knew what water was placed in my hands. The labels, with the names of the localities written upon them, had been tied up, all information regarding the source of the water being thus held back. The bottles were simply numbered, and not till all of them had been examined and described, were the labels opened, and the locality and sea-colour corresponding to the various specimens ascertained. The home observations, therefore, must have been perfectly unbiased, and they clearly establish the association of the green colour with fine suspended matter, and of the ultra-marine colour, and more especially of the black-indigo hue of the Atlantic, with the comparative absence of such matter.

"So much for mere observation; but what is the cause of the dark hue of the deep ocean? A preliminary remark or two will clear our way toward an explanation. Colour resides in white light, appearing when any constituent of the white light is withdrawn. The hue of a purple liquid, for example, is immediately accounted for by its action on a spectrum. It cuts out the yellow and green, and allows the red and blue to pass through. The blending of these two colours produce the purple. But while such a liquid attacks with special energy the yellow and green, it enfeebles the whole spectrum. By increasing the thickness of the stratum we may absorb the whole of the light. The colour of a blue liquid is similarly accounted for. It first extinguishes the red; then, as the thickness augments, it attacks the orange, yellow, and green in succession; the blue alone finally remaining. But even it might be extinguished by a sufficient depth of the liquid.

"And now we are prepared for a brief, but tolerably complete, statement of that action of sea-water upon light to which its owes its darkness. The spectrum embraces three classes of rays—the thermal, the visual, and the chemical. These divisions overlap each other; the thermal rays are in part visual, the visual rays in part chemical, and *vice versa*. The vast body of thermal rays lies beyond the red, being invisible. These rays are attacked with exceeding energy by water. They are absorbed close to the surface of the sea, and are the great agents in evaporation. At the same time the whole spectrum suffers enfeeblement; water attacks all its rays, but with different degrees of energy. Of the visual rays, the red are first extinguished. As the solar beam plunges deeper into the sea, orange follows red, yellow follows orange, green follows yellow, and the various shades of blue, where the water is deep enough, follow green. Absolute extinction of the solar beam would be the consequence if the water were deep and uniform. If it contained no suspended matter, such water would be as black as ink. A reflected glimmer of ordinary light would reach us from its surface, as it would from the surface of actual ink; but no light, hence no colour, would reach us from the body of the water. In very clear and deep sea-water this condition is approximately fulfilled, and hence the extraordinary darkness of such water. The indigo, already referred to, is, I believe, to be ascribed in part to the suspended matter, which is never absent, even in the purest natural water; and in part to the slight reflection of the light from the limiting surfaces of strata of different densities. A modification of light is thus thrown back to the eye, before the depth necessary to absolute extinction has been attained. An effect precisely similar occurs under the moraines of glaciers. The ice here is exceptionally compact, and, owing to the absence of the internal scattering common in bubbled ice, the light plunges into the mass, where it is extinguished, the perfectly clear ice presenting an appearance of pitchy blackness. (I learn from a correspondent that certain Welsh tarns, which are reputed bottomless, have this inky hue).

"The green colour of the sea has now to be accounted for; and here, again, let us fall back upon the sure basis of experiment. A strong white dinner-plate had a lead weight securely fastened to it. Fifty or sixty yards of strong hempen line were attached to the plate. My assistant, Thorgood, occupied a boat, fastened as usual to the davits of the *Urgent*, while I occupied a second boat nearer the stern of the ship. He cast the plate as a mariner heaves the lead, and by the time it reached me it had sunk a considerable depth in the water. In all cases the hue of this plate was green. Even when the sea was of the darkest indigo, the green was vivid and pronounced. I could notice the gradual deepening of the colour as the plate sank, but at its greatest depth, even in indigo water, the colour was still green. (In no case, of course, is the green pure, but a mixture of green and blue).

"Other observations confirmed this one. The *Urgent* is a screw steamer, and right over the blades of the screw was an orifice called the screw-well, through which one could look from the poop down upon the screw. The surface-glimmer, which so pesters the eye, was here in a great measure removed. Midway down, a plank crossed the screw-well from side to side; on this I placed myself and observed the action of the screw underneath. The eye was rendered sensitive by the moderation of the light; and, to remove still further all disturbing causes, Lieutenant Walton had a sail and tarpaulin thrown over the mouth of the well. Underneath this I perched myself on the plank and watched the screw. In an indigo sea the play of colour was indescribably beautiful, and the contrast between the water, which had the screw blades, and that which had the bottom of the ocean, as a background, was extraordinary. The one was of the most brilliant green, and the other of the deepest ultra-marine. The surface of the water above the screw-blade was always ruffled. Liquid lenses were thus formed, by which the light was withdrawn from some places and concentrated upon others, the water flashing with metallic lustre. The screw-blades in this case played the part of the dinner-plate in the former case, and there were other instances of a similar kind. The white bellies of porpoises showed the green hue, varying in intensity as the creatures swung to and fro between the surface and the deeper water. Foam, at a certain depth below the surface, was also green. In a rough sea the light which penetrated the summit of a wave sometimes reached the eye, a beautiful green cap being thus placed upon the wave, even in indigo water.

"But how is this colour to be connected with the suspended particles? Take the dinner-plate which showed so brilliant a green when thrown into indigo water. Suppose it to diminish in size, until it reaches an almost microscopic magnitude. It would still behave substantially as the larger plate, sending to the eye its modicum of green light. If the plate, instead of being a large coherent mass, were ground to powder sufficiently fine, and in this condition diffused through the clear sea-water, it would also send green to the eye. In fact, the suspended particles which the home examination reveals act in all essential particulars like the plate, or like the screw-blades, or like the foam, or like the bellies of the porpoises. Thus I think the greenness of the sea is physically connected with the matter which it holds in suspension. . . .

"At some distance below the Whirlpool Rapids we have the celebrated whirlpool itself. Here the river makes a sudden bend to the north-east, forming nearly a right angle with its previous direction. The water strikes the concave bank with great force, and scoops it incessantly away. A vast basin has been thus formed, in which the sweep of the river prolongs itself in gyratory currents. Bodies and trees which have come over the falls are stated

circulate here for days without finding the outlet. From rious points of the cliffs above this is curiously hidden. he rush of the river into the whirlpool is obvious rough; and though you can imagine the outlet must be sible if one existed, you cannot find it. Turning, owever, round the bend of the precipice to the north-st, the outlet comes to view.

To be continued).

CANADIAN MISSION IN LONDON.

: may be of interest to our readers to have some information as to the constitution and activities of the anadian Mission, which has recently been established in ondon at 1, Regent Street, S.W. 1, by the Dominion overnment.

The Mission was constituted by an Order of the anadian Privy Council in November, 1918, and Mr. loyd Harris was appointed Chairman of the Mission. r. Harris is a Canadian business man who has a wide owledge of the New Industrial Canada, which is one of e products of the Great War. He rendered invaluable rvice to the Dominion and to the Allied cause as head the Canadian War Mission in Washington, and it was the personal request of Sir Robert Borden, the Canadian emier, that he consented to undertake his present ities.

The objects of the Mission are briefly :—

(a). The serious tonnage position arising out of the r coupled with the numerous restrictions put in force, th in the United Kingdom and in Canada, on import d export trade, tended to sever numerous old connecns which had existed for generations between the other Country and the Dominion. It is one of the ies of the Mission to study the question at first-hand l to devise the means of re-establishing the traditional de.

b) A great work of reconstruction and re-organisation st be undertaken in Europe during the next few years order to repair the devastating effects of the war. Raw terials, &c., will be necessary for this work, and many icles required can be obtained from Canada. The ssion hopes, by means of negotiations with the Governnts of the countries concerned, to make arrangements the supply of such goods to the advantage of all intets involved. It is further considering how by a system credits to assist the Governments in purchasing the terials.

:). The Mission is convinced that the resettlement of ope is largely dependent on sufficient supplies of food ng available and distribution being properly organised. food can only be obtained in two ways:—(1) By ims from countries having margins for export; (2) By eased production in Europe itself.

nada has large supplies which she is willing to place e disposal of Europe, and, moreover, by reason of act that she has always specialised in the manufacture gricultural machinery and implements, she is in a ion to come to the assistance of the nations of Europe eir endeavours to produce supplies within their own rs.

addition to foodstuffs of every description, Canada vailable for export the following goods:—Paper and Manufactures; Lumber; Wood Manufactures, ing wood Pulp; Automobiles and other vehicles; ine Launches; Drugs and medicinal chemicals; er and Leather Manufactures; Hides; Aluminium; m Carbide; Asbestos; Iron and Steel Manufac- Copper; Gold Quartz; Silver; Flaxseed; Nickel; Clothing; Furs; Agricultural Implements.

da seeks above all things to develop a larger interof trade with the Mother Country and, indeed, parts of the Empire. Canada has large markets to offer British manufacturers, for she is a large buyer. Canada, too, feels that she can supply to this country many of the materials and manufactures which formerly were bought by Britain from the Central Powers.

The offices of the Mission are at 1, Regent Street, S.W. 1, and its personnel includes, besides Mr. Lloyd Harris, several other prominent Canadian business men who are well acquainted with the present industrial and economic position in Canada. They will at all times be willing to advise persons in the United Kingdom desirous of obtaining information with regard to Canadian Trade.

ORDERS OF THE MINISTRY OF MUNITIONS.

Copper Sulphate.

With reference to the Copper Sulphate Order, 1918, dated February 15, 1918, the Minister of Munitions hereby orders as follows: —

1. The operation of the said Order is hereby suspended on and after April 15, 1919, until further notice.

2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension or any proceeding or remedy in respect of such penalty or punishment.

3. This Order may be cited as the Copper Sulphate (Suspension) Order, 1919.

Blast-furnace Dust.

In reference to the Blast-furnace Dust Order, 1917, dated August 7, 1917, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Order is hereby suspended on and after April 30, 1919, until further notice.

2. Such suspension shall not affect the previous operation of the said Order, or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension, or any proceeding or remedy in respect of such penalty or punishment.

3. This Order may be cited as the Blast-furnace Dust (Suspension), Order, 1919.

Gas Works Retort Carbon.

In reference to the Gas Works Retort Carbon, &c., Control Order, 1918, dated April 19, 1918, the Minister of Munitions hereby orders as follows: —

1. The operation of the said Order is hereby suspended on and after the date hereof until further notice.

2. Such suspension shall not affect the previous operation of the said Order or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Order prior to such suspension or any proceeding or remedy in respect of such penalty or punishment.

5. This Order may be cited as the Gas Works Retort Carbon, &c., Control (Suspension) Order, 1919.

Nitrate of Soda.

The Minister of Munitions announces that the control of Nitrate of Soda will be suspended as on and from May 15, 1919. Transactions will be governed by the present licensing system until May 15, 1919. General licences will, however, be issued on application from now till May 15, 1919, authorising the holders of such licences to deal in Nitrate of Soda, but such licences will not authorise the holders to enter into any transaction which involves the actual movement of Nitrate except within the British Isles before May 15, 1919.

All applications for licences should be addressed to the Ministry of Munitions (Department of Explosives Supply), Storey's Gate, S.W. 1.

NOTICES OF BOOKS

The Applications of Electrolysis in Chemical Industry. By ARTHUR J. HALE, Bc S., F.I.C. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1918. Pp. ix+148. Price 7s. 6d. net.

THIS monograph gives a complete outline of the eletrolytic methods used in chemical industry, which are continually increasing in number and importance. A short account is provided of the general principles of electrolysis, with definitions of the terms and units employed, and there is also a chapter on methods of generating the current, including primary and secondary cells and generators. Thus the student who knew practically nothing of electrical work could get a sufficient knowledge from the book to enable him to understand the subsequent chapters which deal with the applications of electrolysis firstly to the refining of metals. Full practical details of costs, &c., are supplied, and although some of these are unavoidably somewhat out of date they give some comparative indication of expenses and yields. The winning of metals is similarly discussed in detail, and a chapter is devoted to the electrolytic production of hydrogen and oxygen. The electrolysis of alkali chlorides is very fully treated, and some stress is laid upon the important developments of this industry which may be expected in the near future. In some cases processes which have been superseded are described if there are important lessons to be learnt from them, and the preparation of many miscellaneous inorganic and organic compounds is included.

Cast Iron in the Light of Recent Research. By WILLIAM HERBERT HATFIELD, D.Met. Second Edition, Revised and Enlarged. London: Charles Griffin and Co., Ltd. 1918. Pp. xvii+292. Price 12s. 6d. net.

AN excellent account of the equilibrium diagram of the iron carbide system is to be found in the early chapters of this well-known book, together with an admirable discussion of the influence of various factors upon the properties of cast iron. The author's accounts and criticisms of all the most important work which has been done in this region are exceedingly valuable, and no metallurgist can do without the book. A useful feature is the excellent appendix, which gives a full alphabetical list of names and terms used in metallurgical literature with both their French and German equivalents, and short explanations and definitions. The many illustrations and photomicrographs also add greatly to the value of the book. In the second edition much new matter has been added, including descriptions of the latest research work upon malleable cast iron. The report on the present position of the malleable castings industry in this country, which was prepared by the author at the request of the Committee of the Iron and Steel Institute for Foundry Practice, and approved by the Committee for presentation to the Ministry of Munitions, is reproduced in full. It is a most comprehensive and authoritative review of the industry, and is a valuable addition to the book.

I Fenomeni Elettro-Atomici sotto l'Azione del Magnetismo. ("Electro-atomic Phenomena under the Action of Magnetism.") By AUGUSTE RIGHI. Bologna: Nicola Zanichelli. Pp. xvi+435. Price 17.50 lire.

THE chief results of Prof. Righi's experimental work on the effect of a magnetic field upon the electric discharge are fully described in this treatise. An introduct[illegible] which might perhaps be regarded as somewhat [illegible] is provided for the general reader, and deals [illegible] tary facts regarding the ether and electric ph[illegible] electric discharge in rarefied gases, the [illegible] gases, &c. Then the effects of a magnetic [illegible] potential necessary to start the discharge are discussed, and a full account is given of the author's theory put forward to account for the observed facts. The study of luminous phenomena, and of the production of ionomagnetic rotations are treated in the following chapters. Many new and interesting facts are described, and an able exposition is given of the author's own theories, though the views of other workers are somewhat inadequately treated. The last chapter is devoted to the phenomena due to the action of a magnetic field upon currents in gases, in electrolytes, and in metals. The book is intended more particularly for readers who have made no special study of physics, and hence the use of mathematics is avoided as far as possible, although for those who wish to follow some of the necessary calculations they are discussed in a series of appendices.

Catalogue of Lewis's Medical and Scientific Circulating Library (including a Classified Index of Subjects, with the names of those authors who have treated upon them). New Edition revised to the end of 1917. London: H. K. Lewis and Co., Ltd., 136, Gower street, and 24, Gower Place, W.C. 1. Price 12s. 6d. net; to Subscribers 6s.

THIS extensive catalogue of books in Lewis's Circulating Library to the end of 1917 cannot fail to be useful. The Classified Index of Subjects is particularly valuable, as it enables one to see at a glance what works are available. It is very complete, occupying over a hundred pages.

NOTES.

ROYAL INSTITUTION.—Next Tuesday, April 29, at 3 o'clock, Prof. A. Keith will give the first of a Course of four Lectures on "British Ethnology—The People of Wales and Ireland." On Thursday, May 1, Dr. H. S. Hele-Shaw will give the first of two Lectures on "Clutches." The Friday Evening Discourse, on May 2, at 5.30 p.m., will be delivered by Prof. J. W. Nicholson on "Energy Distribution in Spectra"; on May 9, Sir George Macartney on "Chinese Turkestan—Past and Present." On Saturday, May 3, at 3 o'clock, Prof. H. S. Foxwell will give the first of two Lectures on "Chapters in the Psychology of Industry."

WE have received a copy of the "Directory of Paper Makers" for 1919, giving an alphabetical list of all the paper makers in England, Scotland, and Ireland, together with the names of paper makers' representatives, paper agents, &c. Much useful information on various subjects, such as watermarks, trade customs, sizes of papers, and paper trade publications, are given. The price of the catalogue is 2s. 6d. net post free in U.K., 2s. 9d. abroad.

IN the *Journal of the Board of Agriculture* for February, 1919, it is pointed out that on account of the extreme wetness of the winter months it will be necessary to apply nitrate or sulphate of ammonia to the crops to make up for the nitrates that have been washed out of the soil. In experiments with the wheat crop at Rothamsted last year it was found that the yield of grain in bushels per acre on undressed soil was 33·9; that produced where a dressing was given of superphosphates and sulphate of ammonia gave 41·3.

THE difficulty in obtaining tin-plate during the war has developed an important industry for the production of [illegible] cardboard. Containers for foodstuffs and [illegible] hitherto been made from tin- [illegible]rdboard rendered waterproof by [illegible] wax and other like materials, [illegible] is a varnish made from bakelite, [illegible] product of carbolic acid with

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formalin, invented by Dr. L. H. Bakeland. The card vessels are coated with this material and stoved, and are thus found to be excellent substitutes for tin as well as being both lighter and cheaper. This manufacture will probably largely replace the familiar tin can.

Mr. William Rudderham, for many years general manager, and since 1915 a director of Coleman and Co., Ltd., Norwich, has been appointed managing director in place of the late Mr. W. C. Snelling.

At the Extraordinary General Meeting of the Chemical Society on May 8 the following resolutions will be proposed:—(1) That women should be admitted to the Society on the same terms as men. (2) That in the election of Officers and Council a postal vote of Fellows resident in the United Kingdom should be taken. (3) That every alteration of the by-laws should require for its adoption a two-thirds majority of those voting. (4) That no alteration of the by-laws should become effective until one month after its adoption has elapsed, within which period it should be competent for not less than thirty Fellows to demand a poll of all Fellows resident in the United Kingdom. (5) That the number of ordinary members of Council should be raised to at least eighteen. (6) That the class of "Associates" should be abolished. (7) That the term "Honorary and Foreign Members" should be replaced by "Honorary Fellows." (8) That the limit placed by the Charter on the yearly value of the Society's premises should be raised. In the event of any or all of the foregoing resolutions being adopted, the following further resolution will be moved:—(9) That the Council be and hereby is empowered to take steps to secure a Supplementary Charter giving the necessary power to alter the by-laws in the sense of the foregoing resolutions.

Mr. W. S. Barclay, of the Federation of British Industries, sailed on Saturday last for South America to act as a Special Commissioner to conduct back to this country the Brazilian Delegates who have been appointed by the Brazilian Government to undertake a tour to this country as the guests of the Federation. Mr. Barclay was attached to the recent Mission to Brazil under Sir Maurice Bunsen, and has therefore had exceptional opportunities of appreciating the problems of Anglo-Brazilian Trade. At the end of the present tour of these Brazilian Delegates the Federation intends to send a permanent Commissioner to Brazil as part of its Overseas Commissioner Service. It will be remembered that the Federation, last autumn, entertained a number of Greek Delegates under the leadership of the Greek Minister of Agriculture and conducted them over many of the largest manufactories in this country. As an outcome of this tour the Federation has arranged a British Industrial Exhibition at Athens in the near future which should prove most beneficial to British Manufacturers. The Federation intends to continue this policy of bringing delegates from abroad to this country and thus fostering in every way friendly relations between British manufacturers and potential customers from all over the world.

The Swiss Trades Exhibition will be held at Basle from April 24 until May 8. This Exhibition was first held at Basle in April, 1917, when the exhibitors numbered 831. In 1918 they increased to 990, and at the third exhibition this month there will be 1300 firms showing their products. In 1917 business to the amount of 20 to 25 million francs was done; last year that amount was doubled. Between two and three hundred thousand visitors attended the first and second exhibitions, and the number of buyers last year was 18,000. It is claimed that the Swiss Trade Exhibition in Basle is not a copy of any foreign exhibition; it enjoys in its present organisation and development a special Swiss character. It aims not only at an increase of the Swiss home trade, but also at an extending of the Swiss exports. The goods offered are purely Swiss, and a strict control is stated to exclude all foreign products from participation in the Swiss Trade Exhibition. The general public are admitted two days in the week, according to the principle: "The Exhibition is a means of communication to connect buyers and exhibitors." The goods offered are divided into the following nineteen groups:—Articles of food and luxuries; Drugs and Chemicals; House and Kitchen utensils, Household goods, Glass and China; Fittings for apartments, Furniture and Basket goods; Heating, Light, and Sanitary fittings; Technical articles in metal, wood, glass, cork, leather, india-rubber, &c.; Office and Shop fittings, Office articles, Drawing and Painting utensils; Paper manufactures and Graphic arts; Musical instruments and Music; Articles of sport and toys; Artistic industrial articles; Clocks, Watches, and Jewellery; Textile Goods, Clothing and Outfitting (boots, leather and celluloid articles, fancy goods, drapery); Machinery and Tools; Fine mechanical instruments, Instruments and Apparatus; Electrical industry; Raw materials and Building materials; Agriculture and Horticulture; Sundries. For the Exhibition of 1919 twice as much ground as last year is required. All buyers, after sending in a written notification for the visit, receive a buyer's card with their name, which is available for two days, but can be renewed if necessary. The buyers' cards are only issued for those genuinely interested. The list of the buyers was closed on April 5, 1919. Prospective visitors who hold credentials from a British Authority, or their Chamber of Commerce, can receive all necessary information by addressing M. Henri Marten, First Secretary of Legation and Commercial Adviser, the Swiss Legation, 32, Queen Anne Street, Cavendish Square, London, W. 1.

Iron and Steel Institute.—*Annual Meeting*, 1919.—The Annual Meeting of the Institute will be held, by kind permission, in the House of the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 8 and 9, 1919, commencing on Thursday at 10.30 a.m., and on Friday at 10 a.m. The following is the programme of the proceedings:—

Thursday, May 8 (*at* 10.30 *a.m.*).

General Meeting of Members.
The Council will present their Report for the year 1918.
The Hon. Treasurer will present the Statement of Accounts for 1918.
Scrutineers will be appointed for the examination of voting papers for the election of new Members and Associates of the Institute.
Award of the Bessemer Medal for 1919 to Prof. Cav. Federico Giolitti, Ph.D. of Turin.
Papers Nos. 6, 8, 3, 16, 17, will be read and discussed.
The Meeting will be adjourned.
Joint Session (by invitation of the Institution of Electrical Engineers) to discuss papers on Electric Steel Furnaces. The following is a list of the papers likely to be submitted:—
"Developments in Iron and Steel Electric Furnaces," by J. Bibby; "The Booth Hall Electric Furnace," by W. K. Booth; "The Development of the Electric Melting Furnace," by D. F. Campbell; "The Control of Electric Arc Furnaces," by H. Coates; New Type of Electric Furnace," by Axel Sahlin; "Large Electric Furnaces," by Victor Stobie.
Members who desire to take part in the discussion can obtain copies in advance on application to the Iron and Steel Institute.

Friday, May 9 (*at* 10 *a.m.*).

General Meeting of Members.
The award of grants from the Andrew Carnegie Research Fund in aid of research work will be announced.
Papers Nos. 11, 10, 1, 2, will be read and discussed.
Afternoon Session to read and discuss papers 15, 7, and 12.

Those papers for which time cannot be found will be taken as read and discussed by correspondence.

The following is a list of Papers that are expected to be submitted :—

1. J. H. Andrew : "Manufacture and Working of High-Speed Steel."
2. J. O. Arnold and F. Ibbotson : "Molecular Constitutions of High-Speed Tool Steels and their Correlation with Lathe Efficiences."
3. C. H. F. Bagley : "Modern Steel Metallurgy."
4. G. Cesàro : "Note on the Liquidus in the Iron-Carbon Diagram."
5. G. Watson Gray : "Estimation of Phosphorus in the presence of Tungsten."
6. L. Greiner : "Report on the Condition of Belgian Iron and Steel Work after the German occupation."
7. D. Hanson and J. E. Hurst : "Improvements in the Case-Hardening Process."
8. L. C. Harvey : "Use of Powdered Coal."
9. K. Honda : "On the Non-Allotropic Nature of the A2 Transformation in Iron."
10. J. C. W. Humfrey : "Macro Etching and Printing."
11. H. M. Howe : "A Review of Work of United States National Research Council."
12. A. McCance : "Carburisation of Iron at Low Temperatures."
13. A. M. Portevin and M. Garvin : "An Experimental Investigation of the Influence of the Rate of Cooling on the Hardening of Carbon Steels."
14. K. Tawara and G. Asahara : "On Graphitisation in Iron-Carbon Alloys."
15. G. Taylor : "Some Points in the Manufacture of Files."
16. J. H. Whiteley and A. F. Hallimond : "The Acid Hearth and Slag."
17. B. Yaneske : "Deoxidation, and the Influence of Lime on Equilibrium in the Acid Open-Hearth Furnace."

NOTES FROM FOREIGN SOURCES

Margarines and their Richness in Butter.—M. W. Arnold.—When margarines were made only of fats and oils possessing a fairly low Reichert-Meissl index it was comparatively easy to deduce the proportion of butter they contained from the index. Now, however, when coco butter and palm nut oil are so largely used for making margarine it has become a much more difficult task. In order to obtain definite information as to the presence of butter in margarine it is necessary to determine—(a) the index of saponification, (b) the Reichert-Meissl index, (c) the Polenske index (of the original fats and the fats treated with alcohol), and (d) the molecular weight of the water-soluble fatty acids. Margarines can then be classed as follows :—(i.). Those containing neither butter nor palm oil. If both the Reichert-Meissl index and the Polenske index of the original fats do not exceed 0·55 neither butter nor palm oil can be present. (ii.) Those containing butter. The absence of palm oil is shown by a low Polenske index, while the presence of butter may be deduced from the high Reichert-Meissl index. The molecular weight of the water-soluble fatty acids lies between 97 and 107 (benzoic acid, which increases the Reichert-Meissl index has a molecular weight of 122). (iii.). Those containing coco-butter. The presence of palm oil is indicated by a Polenske index above 0·6 and molecular weights of the soluble fatty acids between 130 and 144. To decide whether coco-butter or palm oil is present it is important to take into account the relation existing between the Reichert-Meissl and Polenske indices. If a little of both is present the physical state of the Polenske acids must be taken into account. (iv.). Those probably containing palm oil. In this case the Polenske index is above 0·6, the molecular weight of the water-soluble acids is between 130 and 136, and the Polenske acids are, if the percentage of palm oil is pretty high, generally solid or semi-fluid, and not clear. (v.). Those containing butter and coco-butter. The Polenske index is higher than 0·55, and often higher than 0·6. The Reichert-Meissl index is relatively higher than in the case of the absence of butter, and the molecular weight of the acids lies between 110 and 130. (vi.). Those containing butter and palm oil. These are characterised by the fact that the Polenske acids are solid, and by the fact that the Polenske index of the fats treated with alcohol is only 2·9.—*Zeitschrift für Untersuchung der Nahrungs und Genussmittel*, xxvii., 379.

New Reagent for Bases and Acids.—Marc Chauvierre.—A decoction of red beetroot is an excellent reagent for bases and acids. It may be prepared by simply boiling pieces of beetroot in water and filtering, when a reddish violet very opalescent liquid is obtained. A drop of potash turns it dark yellow, while mineral acids and even the weakest organic acids turn it back to its original colour. The reagent is very sensitive, a solution of 1 grm. of boric acid in a litre of water reddening it very decidedly, after it had been decolorised by lime. The reagent cannot be used in the form of paper, as it is not readily fixed on paper. It does not appear to be a true solution but a colloidal hydrosol.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 118.

Diffusion of Light by Molecules of Air.—J. Cabannes.—In 1914 the author undertook an experimental study of the diffusion of light by molecules of gas, and showed that it was possible to observe light diffused by some cc. of air, freed from dust, in normal conditions of temperature and pressure. These researches, which were confirmed by Strutt, were interrupted by the war. Wood has recently thrown doubt upon these results, and suggests that the observed diffusion might be due to mist produced in the air by ultra-violet radiations. The author now points out the precautions that must be taken in order to do away with disturbing phenomena. It is clear that certain ultra-violet radiations may introduce complications in the study of light diffused by gases, and in order to verify Lord Rayleigh's theory experimentally it is best to exclude radiations of wave-length below 0·3μ. By a photographic method, however, it is possible to study the diffusion of radiations of high frequency by molecules of air. It is necessary to illuminate only a small part of the gaseous mass contained in a closed vessel, and that only for very short periods (ten to thirty seconds) separated by fairly long intervals (ten to thirty minutes).—*Comptes Rendus*, 1919, clxviii., 340.

Influence of Light upon the Absorption of the Organic Matter of the Soil by Plants.—Dolorès Celian de Besteiro and M. Michel-Durand.—In 1911 Cailletet pointed out that certain plants live normally in light which appears to be too faint to enable them to assimilate carbon dioxide sufficiently from the air, and he suggested that these plants, being unable to obtain all the carbon they require from the air, might derive a considerable amount from the soil in the form of organic matter. The authors have taken up the question, experimenting for the purpose with a plant which is a heliophite, viz., *Pisum sativum*. They grew the plants in a culture consisting of Knop's liquid, containing 4 parts per thousand of glucose, and exposed them to varying intensities of illumination. From determinations of the increase of dry weight of the plants, the glucose absorbed by each plant, the glucose absorbed per grm. of dry weight of the root, and that absorbed per grm. of dry weight of the entire plant the following conclusions could be drawn :—(i.). The plants increased more in weight the more intense the illumination to which they were exposed. (ii.). The roots also were better developed in stronger illuminations. (iii.). The plants which grew in a more intense light absorbed more glucose. (iv.). The same weight of root absorbed decidedly more glucose in faint than in strong lights. (v.) The same

weight of whole plant absorbed practically the same amount of glucose in illuminations of different intensities. This last conclusion shows that the plant is incapable of augmenting the absorbing power of its roots so that they can extract more organic carbon from the soil. Thus there is neither parallelism nor compensation between the absorption of carbon by the green leaves in the carbon dioxide of the air and the absorption of organic carbon from the soil by the roots.—*Comptes Rendus*, 1919, clxviii., 467.

Discovery of a New Glucoside "Loroglossine."—Em. Bourquelot and M. Bridel.—The authors have applied the biochemical method of investigation to various indigenous kinds of orchids, *e.g.*, *loroglossum*, *orchis*, *ophrys*, &c. In one of these (*L. hircinum*) they have discovered a new glucoside, to which they have given the name "Loroglossine." The aqueous extract of the plant was exposed successively to the action of invertine (reagent for cane sugar) and emulsine (reagent for glucosides). They found that the plant, like all phanerogams, contains cane sugar. It also contains a glucoside hydrolysable by emulsine and a fairly large proportion of a dextrogyratory principle, which is not attacked by ferments, for after the action of the invertine the liquid is still dextrorotatory, while the glucoside not yet hydrolysed is lævorotatory. Loroglossine crystallises in long colourless needles; it is odourless and very bitter; very soluble in water and alcohol, very slightly soluble in acetic ether and acetone. It is lævorotatory, does not reduce cupric liquid, and is hydrolysed by warm dilute sulphuric acid, as well as by emulsine.—*Comptes Rendus*, 1919, clxviii., 701.

Researches on Chemical Luminescence.—J. Lifschitz.—The study of the emission of light in chemical reactions, like that of the absorption and chemical effects of light, may lead to important results concerning the connection between radiant and chemical energy and the nature of chemical forces. The phenomenon of chemical luminescence has been observed in many reactions, and not by any means in oxidation processes only. For example, a beautiful luminescence appears when hydrobenzamide is distilled in a current of hydrogen, lophin being the product, while various decompositions of unknown nature occur simultaneously. Thus the reaction is essentially an intramolecular transposition. Other reactions show that the appearance of chemical luminescence is not dependent either upon the total amount of energy transformed or upon the velocity of the reaction. For instance, nitrogen dioxide acts at least as energetically upon phenyl magnesium bromide as air, but it is only with the latter that chemical luminescence is observed, and then only in absence of moisture. It has been shown that when ethereal Grignard's solutions react with oxygen chemical luminescence appears in the case of aromatic organo-metallic compounds, but not with aliphatic compounds, this difference being due to the different stability of their etherates. The same phenomenon is observed with the addition products of organo-magnesium compounds with dimethyl aniline. The total liberation of heat in the formation of etherates seems to be less with the aromatic Grignard compounds than with the aliphatic compounds.—*Helvetica Chimica Acta*, 1918, i., 472.

MEETINGS FOR THE WEEK.

TUESDAY, 29th.—Royal Institution, 3. "British Ethnology—The People of Wales and Ireland," by Prof. A. Keith.

THURSDAY, May 1st.—Royal Institution, 3. "Clutches," by Dr. H. S. Hele-Shaw.

— Royal Institution, 5. (Annual Meeting).

— Institution of Electrical Engineers, 6. "Magnetic Storms," by Dr. C. Chree.

FRIDAY, 2nd.—Royal Institution, 5.30 "Energy Distribution in Spectra," by Prof. J. W. Nicholson.

SATURDAY, 3rd.—Royal Institution, 3. "Chapters in the Psychology of Industry," by Prof. H. S. Foxwell.

Assayer, aged about 25, with knowledge of Gold and Silver Assaying, required at once. Permanent position; good prospects; Birmingham. State age, experience, and salary required.—Address, "A. 25," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Assistant Chemist desires Position in a Laboratory. Has had two years' experience in Acid Analyses, and also two years' Inorganic Chemistry and Qualitative Analyses in College. Would commence at moderate salary.—Address, Mr. J. Parkes, 13, Clarence Road, Ponders End, Middlesex.

CHEMIST.—Wanted for Factory Testing work, qualified Analytical Chemist.—Apply, giving full particulars, to Manager, The Imperial Tobacco Co., Ltd., Dingley Road, City Road, E.C. 1.

Discharged Soldier desires Situation in Chemical Laboratory. Specially qualified in Metallurgical Analysis of Rare Metals.—Address, D. S., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Enterprising Assistant Chemist (21) desires a Position in a Laboratory or Works. Formerly Assistant Chemist, Directorate of Chemical Inspection, and capable of undertaking any Inorganic Analyses. Would commence at moderate salary. —Address, Mr. W. G. Richards, 7, Sivell Place, Heavitree, Exeter.

Junior Chemist (20), Inter. B.Sc. (Lond.), previous experience, seeks Situation in London Laboratory or Works.—Address, L. L., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Laboratory Attendant, having a fair knowledge of General Chemistry and good experience, wanted. State wages required and full particulars.—Address, "Investigator," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Two Analytical Chemists are required for a large Testing Laboratory. Commencing salary £200 per annum. It is desired that applicants should have had at least two years' experience in the Laboratories of Steel or other Metallurgical Works. Preference given to those who have *fought in the War.* —Address, "Analytical," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3081.

THE ANALYSIS OF SAUSAGES, MEAT PASTES, AND ARMY RATIONS.

By A. W. STOKES, F.I.C.

Sausages.—While the "Food Control Regulations" lay down qualities and prices for sausages, requiring that the meat should be, for one price, 50 per cent and, for another price, 67 per cent by weight, it is necessary to be able to determine these limitations. Having analysed over 60 samples a description of the method I have used may be of interest.

The main constituents of sausages are meat, bread, and water. A little salt and spice are usually added. Whilst the meat may be derived from any part of the animal it is, of course, in most cases impossible to determine either the animal or the part used.

The water is the chief difficulty. In the following analyses of all meat products I have assumed that meat naturally contains 70 per cent and bread 40 per cent of water. The meat is dissolved by boiling in alcoholic soda solution, with formation of a soap from the fat. The insoluble matter is then placed in an aqueous caustic soda solution to dissolve the starch, which is then precipitated by strong alcohol.

The actual method used is as follows:—The total solids, water, and ash are estimated in the usual way on 5 grms. of the material. Boric acid may be looked for in the ash. Ten grms. are boiled for one hour in alcoholic (methylated) solution of caustic soda (the alcohol being of at least 90 per cent, and the caustic soda of 5 per cent strength) under a reflux condenser. This treatment should dissolve the meat, form a soap with the fat, and leave the starch unaltered. This is filtered while hot through a small plug of slag-wool, and washed with strong hot alcohol. The filtrate is cooled and made up to 250 cc. with water, and 25 cc. evaporated to about 15 cc. (to remove the alcohol). The fatty acid is determined in this, using the Schmid method as in milk analysis. The filter-plug and residue are returned to the original flask; about 100 cc. of cold aqueous 5 per cent soda solution are added and left for one hour, with occasional shaking. This will dissolve the starch. The volume is made up to 500 cc. with cold water and filtered through a small slag-wool plug. Fifty cc. are collected, and about 100 cc. of strong alcohol (90 per cent) are added to precipitate the starch; after stirring and allowing to stand for half-an-hour the starch is filtered through counterpoised filter-papers, washed with alcohol, dried, and weighed. The filtrations are sometimes difficult, but may easily be managed without a filter-pump if a filter-flask be used to which is attached a short piece of rubber tube; mouth suction is applied to the end, the tube doubled over, and a clip applied to the part doubled.

Calculation.—The fatty acids may be assumed to equal 95 per cent of actual fat. From the total solids are subtracted the starch and fat to get, by difference, the dry meat. To this "dry meat" is added 2·33 times its weight of water; this will give the fat-free flesh (called "flesh" in the following tables). To the starch is added 0·[illegible] times its weight of water to form bread.

Frequently it will be found that the water actually present is above the quantities allowed by this calculation. This is due to the fact that in the manufacture of sausages the crusts and the bread used are soaked in water to soften them, and this water is only partially squeezed out before being chopped up with the meat. Very rarely the bread or the meat may contain less than the amounts I have allowed for water. The ash consists mainly of salt, though in 12 out of 60 samples analysed boric acid was also present, but in small amounts. The total ash varied from 1·2 to 3 per cent, with an average of 2 per cent.

The results obtained from the five following samples may be of interest; they are selected (Table I.) as showing mainly the extremes of each ingredient.

TABLE I.—*Sausages.*

Per cent.	No. 1.	No. 2.	No 3.	No. 4	No. 5.	Average of 60 samples.
Fat	0·9	20·2	9·5	6·9	20·9	11·2
Bread	9·5	16·7	5·3	32·2	29·4	20·3
Flesh	89·1	72·2	71·0	51·1	26·0	60·2
Water present	66·8	48·1	66·0	58·4	53·6	58·6
Water allowed	66·3	57·2	51·8	48·6	29·9	50·3
Water excess..	0·5	—	14·2	9·8	23·7	8·3

The smallest amount of water found to be present was 48 per cent (No. 2); this sample it will be observed sums up to 109·1 per cent. This and three other samples were the only specimens showing that the meat and the bread contain less than the calculated allowances of water. No. 5, which contained the largest excess of water (23·7 per cent), was seen by microscopical examination to consist largely of tripe.

In only a few cases were these samples examined microscopically; usually the indications were not particularly useful. Some few were analysed before and after cooking; generally the amounts of water and of fat diminished after cooking. But, as no standard for water could be assumed for these, the results are of little interest, and are not recorded here.

Meat Pastes.—Meat pastes, variously described as ham and chicken, tongue and chicken, veal and ham, ham and tongue, ham, tongue, and chicken, turkey and tongue, and wild duck, prepared by various makers, were analysed in the same way. The results of 14 of these show for the extreme percentages of each of the ingredients (Nos. 1 to 5), and the averages for all are given in Table II.

TABLE II.

Per cent.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	Average of 14 samples.
Fat	3·6	16·6	15·4	13·4	11·1	13·2
Bread	11·0	3·0	6·7	13·8	13·6	8·7
Flesh	61·0	85·3	63·2	45·1	41·1	63·6
Water present	71·6	55·9	61·6	65·0	69·0	62·6
Water allowed	47·0	60·9	46·9	37·3	34·2	48·1
Water excess..	24·6	—	14·7	27·7	34·8	14·5

The only sample out of these 14 that summed up to over 100 was No. 2, which, on the allowances for water in the flesh and bread, totalled to 104·9 per cent. This was in every respect far above all the other samples, containing the least amount of bread and no excess of water. On reference to the maker I was informed that my results were within 2 per cent of the materials used.

Of the samples the highest ash was 5·28 per cent, but this was mainly due to common salt; the lowest was 1·48, the average 2·9 per cent. No boric acid was present in any of these.

To see how the process would work in various hands Messrs. G. A. Stokes and E. W. Wright kindly analysed a few samples of sausages for me. Their results were very similar to mine, as shown by the example Table III.

TABLE III.

Per cent.	G. A. S. and E. W. W.	A. W. S.
Fat	14·5	14·2
Bread	28·0	27·8
Flesh	39·5	41·0
Water excess	18·0	17·0

Army Rations.—A number of army rations were examined to see if they complied with the contract

specifying them to contain not more than 12 per cent fat, or 170 per cent water, or more than 2 grains of tin per pound. They were not to have a greater acidity than the equivalent of 72 cc. of N/10 soda in 100 parts. They consisted of mixtures of meat, potato, haricot beans, peas, carrots, and onions cooked in sealed tins.

It was found easiest to pick out all the meat separately and to shred this finely. The vegetables could readily be mashed and mixed in the tin, the meat then added, and the whole well incorporated in the same tin so as to absorb any moisture therein. The analyses of these were performed as in the case of the sausages, omitting, however, any estimation of starch.

For the acidity, 5 grms. were shaken with 100 cc. of cold water for one hour; an aliquot part was then titrated, after filtration, with N/10 soda. The results of 5 samples are appended (Table IV.).

TABLE IV.

Per cent.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	Average.
Fat	11·7	4·9	8·2	8·2	8·1	8·2
Water ..	67·5	73·0	67·4	68·0	68·4	68·8
Acidity ..	16·0	32·0	48·0	32·0	30·0	31·6
Ash	1·2	1·3	1·4	1·3	1·6	1·4

Only in one case (No. 2) was the amount of water slightly beyond the limit. In no case was any tin or boric acid detected.

A review of the results of the analyses of the sausages and meat pastes shows that an excess of water, not natural to the meat and bread, may in the sausages reach about 24 per cent, and in the meat pastes 35 per cent. This high excess is usually due to the use of much bread; this soaked in water enables a large amount to be incorporated.

In the United States the use of any starchy matter in sausages is forbidden. It is to be regretted that such is not the case in England. A sample like sausage No. 5, which contains about equal parts of fat (21 per cent), meat (26 per cent), bread (29 per cent), and excess water (24 per cent), would not be possible were it illegal to use bread.

I am greatly indebted to Mr. G. W. Bender for his assistance in this work.

DISCUSSION.

The PRESIDENT, in opening the discussion, said that the Minis ry of Food had consulted the Society in reference to the carrying out of their Sausage Orders under the following circumstances:—On January 21, 1918, the Department found it necessary to introduce the meatless days, and in that Order, known as the Public Meals Order, the expression "meat" was deemed to include sausages. In February the Meat Licensing Order was issued which forbade any person after March 15 from dealing in dead meat without a licence, and in this Order sausages were included as dead meat. This was revoked in Ireland on June 17, but later in the year the Ministry again issued an Order in which they then fixed the price of sausages according to their meat content, ignoring the fact that sausages were supposed by the previous regulations to be all meat. Pork sausages had also not been included in their Pig and Pig Products (Prohibition of Export) Order, as only bacon, ham, and lard were included in it. The Government Laboratory had tried to solve the mystery of what is now meant by a sausage of different grades, and the Society was glad to welcome their contribution to the discussion.

Dr. VOELCKER suggested that it would be better if the Ministry of Food and other Government Departments, before making their Orders and putting out regulations as to how mixed foods should be compounded, would consult analysts generally and the Government Laboratory in particular as to whether it was possible to ascertain by analysis whether the composition could be ascertained, and not wait, as was here done in the instance of sausages, &c., to hear the difficulties expressed at a subsequent meeting of this Society.

It seemed to him that the authors of the papers they heard read relied mainly upon the amount of nitro shown in the analysis, and reckoned this as represen the meat present. He would like to ask what w happen if he sprinkled a little sulphate of ammonia ov sausage or mixed some leather powder with it—would be reckoned as "meat"?

He had heard no mention of microscopical analysi this connection, and thought that it should be emplo The inclusion of soya bean meal, for instance, coul so detected.

Mr. CRIBB inquired if the Food Controller had dr up any definition of "meat," as the value of the meth proposed in the two papers under discussion must lar depend on what was meant by that word.

In pre-war days he had had occasion to examine s sausages which consisted almost entirely of fat and br with a little connective tissue and only a trace of mu fibre. Would such a mixture comply with the "Order

An ingenious manufacturer might put a large pro tion of gristle and connective tissue into his sausage m This, owing to the low nitrogen factor for gelatin as c pared with that for proteins, would seriously affect figure for "flesh" obtained by the method recomme by Messrs. Stubbs and More. The presence of anyt like a substantial proportion of liver, owing to the glyc present, would give trouble in other directions.

In view of these difficulties he would like to s number of analyses, by the methods now put forwar sausages of known composition, as by this means would it be possible to decide whether the problem se the Ministry of Food could be satisfactorily solved. any case he thought that the analytical figures obta would have to be interpreted with great caution, ar would be quite unsafe to take action in cases anyw near the border-line.

With regard to sausage skins, to which the Presi had referred, some years ago he was consulted abo large consignment of sausages which on being ser America were refused admission to that country, on ground that they contained boric acid. The manufactu had put in none, and he was quite unable to find an the sausages as a whole; but it transpired that authorities in America had actually examined the s separately, and had found an extremely minute trac boric acid, which on examining a number of the skin afterwards ascertained to be between one and two p per million.

The skins before use were kept in a saturated salt s tion, and this was the only apparent source from whic boric acid could have been derived. Skins kept in way would presumably be sterile.—*The Analyst*, x No. 517, p. 127.

PHYSICAL CHEMISTRY AND ITS BEARIN ON THE CHEMICAL AND ALLIED INDUSTRI

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc

(Continued from p. 197).

THE systematic study of homogeneous catalysis has to very definite and interesting results, some of which be illustrated by a couple of examples. The first of t refers to the influence of the *concentration* of the cata and is based on a study of the rate at which diazoam benzene is converted into aminoazobenzene. This ch takes place in aniline solution when an aniline salt, ac as catalyst, is present. The course of the reaction ca followed quantitatively, and the rate of change is ex sible by a velocity coefficient, the value of which vari

* Cantor Lecture (II.). Delivered before the Royal Society of December 9, 1918. From the *Proceedings of the Royal Society of* lxvii., No. 3451.

direct proportion to the concentration of the catalyst, other conditions being unaltered. This is apparent from the figures given in Table IV.

TABLE IV.—*Diazoaminobenzene* $\rightleftharpoons$ *Aminoazobenzene.*

Concentration of aniline hydrochloride.	Velocity coefficient at 25°.
0·1	0·0060
0·2	0·0123
0·3	0·0180

Again, in cases of homogeneous catalysis it is possible to compare the efficiency of different catalysts under given conditions. The change of cane-sugar, for example, into invert sugar takes place with appreciable rapidity in presence of an acid as catalytic agent, and can easily be followed with a polarimeter. The course of the reaction is in harmony with the formula for a unimolecular reaction; *i.e.*, the velocity coefficient $k = \frac{1}{t} \cdot \log_e \frac{a}{a-x}$. This will be seen in Table V.

TABLE V.—*Inversion of Cane sugar by* N/2 HCl *at* 25°.

t minutes.	Angle of rotation.	$\frac{1}{t} \log_e \frac{a}{a-x}$.
0	+25·16°	—
56	16·95°	0·00501
116	10·38°	0·00501
176	5·46°	0·00504
236	1·85°	0·00504
371	−3·28°	0·00508
∞	−8·38°	—

Now it is found that the rate of inversion of cane-sugar at a given temperature in presence of acid of a definite normality varies notably with the nature of the acid. Thus the catalytic efficiency of hydrochloric acid in promoting the inversion of sugar is greater than that of sulphuric acid and acetic acid at the same temperature and the same concentration, and, indeed, for N/2 concentration, the velocity coefficients obtained in the three cases stand in the ratio 100:54:0·4. So far, then, as homogeneous catalysis is concerned, the evaluation of velocity coefficients provides a rational method of comparing the activity of different catalysts under the same conditions.

The majority of the technically important catalytic reactions belong, however, to the "heterogeneous" class, and in these cases the application of the reaction velocity formulæ already discussed and illustrated cannot be carried through to anything like the same extent. Indeed, the careful study of cases of heterogeneous catalysis on quantitative lines reveals the fact that other factors are operative besides mass action. This is brought out very clearly, for example, by Bone and Wheeler's research on the combination of hydrogen and oxygen at hot surfaces.

In this work provision was made for the circulation of hydrogen and oxygen through a tube packed with fragments of unglazed porcelain and maintained at a constant temperature, the gradual combination of the gases which took place under these conditions being followed quantitatively by determinations of the pressure from time to time. Plainly, as the reaction $2H_2 + O_2 = 2H_2O$ proceeds, the pressure falls regularly, and provides a record of the progress of the change. From such a record the velocity of combination of the gases may be calculated.

On the ground that two distinct substances disappear during this reaction it might fairly be expected that the course of the change would conform to the bimolecular or the trimolecular type. The surprising result, however, has emerged that the rate of reaction is represented by the unimolecular formula. In support of this the figures in Table VI., obtained with normal electrolytic gas at 450°, may be quoted:—k_1 is the velocity coefficient calculated by the unimolecular formula, k_2 is that based on the bimolecular formula.

TABLE VI.

t hours.	Pressure in mm.	k_1.	$k_2 \times 10^6$.
0	465·6	—	—
12	324·0	0·0131	78·2
24	228·6	0·0129	92·8
36	163·9	0·0126	109·8
48	116·1	0·0125	134·7
72	60·7	0·0123	199·0
96	28·6	0·0126	341·8
120	14·6	0·0125	552·7

Experiments were made also in which the initial mixture contained hydrogen and oxygen in other than the volume ratio 2:1, and in which the partial pressures of the separate gases were ascertained at each stage, as well as the total pressure. A unimolecular constant was then calculated for the rate of disappearance of each gas separately, viz., k_{H_2} and k_{O_2}, and it was found that the former alone was constant. This important result may be illustrated by the figures obtained with a mixture of 3 volumes of hydrogen with 1 volume of oxygen, circulated over porcelain at 430°. The quantities P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen at the successive stages (Table VII.).

TABLE VII.

t hours.	P_{H_2} mm.	P_{O_2} mm.	k_{H_2}.	k_{O_2}.
0	292·5	94·9	—	—
2	260·5	78·9	0·0253	0·0401
4	230·5	63·9	0·0259	0·0429
6	206·2	51·8	0·0253	0·0438
8	185·9	41·7	0·0246	0·0447
12	151·8	24·6	0·0237	0·0488
16	123·6	10·4	0·0240	0·0600

From these and other figures it appears that the rate of change is proportional to the partial pressure of the hydrogen, and this must mean, as Bone has pointed out, that the formation of steam is an indirect process, dependent on a primary change, at the surface of the catalyst, in which hydrogen is concerned. The evidence favours the view that the catalytic action of porcelain depends on the occlusion of the reacting gases on its surface, and the results quoted above indicate that the rate of change is determined mainly by the rate of occlusion of the hydrogen. Hence in studying the catalysis of hydrogen and oxygen at hot surfaces it is not really the velocity of a chemical reaction that is being measured, but the rate of a purely physical process. The operation of the law of mass action is masked, and it may be that the chemical combination of the hydrogen and the oxygen at the surface of the catalyst is exceedingly rapid, perhaps instantaneous.

The investigations to which reference has just been made laid the foundations for the introduction of what is known as "surface combustion," in which the catalytic effect of hot surfaces in promoting combustion receives practical application. A homogeneous explosive mixture of inflammable gas and air is made to burn without flame in contact with a granular solid, the latter acting as an accelerator of the combustion, and becoming itself incandescent. In various ways, a description of which would lie outside the scope of these lectures, this surface combustion may be employed for such purposes as the concentration and evaporation of liquids, for heating muffle furnaces, and for steam raising.

In another field, lying far apart from that of combustion, heterogeneous catalysis is found to present various features which are foreign to the law of mass action. Some of the most important catalytic reactions, including many of technical significance, are those which take place under the influence of enzymes. These are catalysts, formed by living organisms and of very complex nature, which promote in a remarkable degree many changes in organic matter. To this class of catalysts belong, for example, invertase, diastase, and the enzymes of yeast.

In certain cases the hydrolysis of carbohydrates under the influence of enzymes is marked by the peculiarity that during the first stages the amount of change is a linear function of the time; *i.e.*, a constant weight of the carbohydrate is hydrolysed in a given interval of time. Such behaviour is not in harmony with the logarithmic mass action formula, $k = \frac{1}{t} \log \frac{a}{a-x}$, which as already shown, does represent accurately the course of hydrolysis of cane-sugar under the catalytic influence of acids.

A case in point is the action of diastase on starch, the earlier portion of the time curve being linear, the later portion being logarithmic in character. This is proved by calculating the velocity coefficient $k = \frac{1}{t} \log \frac{a}{a-x}$, (1) for each observation from the start of the reaction, (2) for each observation after the linear portion of the time curve has been passed, a new starting-point being chosen. A comparison of two sets of values of k obtained in this manner is given in Table VIII., which refers to the hydrolysis of a 3 per cent starch solution by malt extract at 51—52°.

TABLE VIII.

Time (min.).	k.	Time in min. from new starting-point.	k.
10	0·00498	—	—
20	0·00553	—	—
30	0·00590	—	—
40	0·00620	0	—
50	0·00650	10	0·00842
60	0·00690	20	0·00831
70	0·00706	30	0·00821
80	0·00728	40	0·00837
90	0·00730	50	0·00818
100	0·00732	60	0·00807
110	0·00749	70	0·00822
120	0·00762	80	0·00840
130	0·00779	90	0·00855

(To be continued).

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Continued from p. 200).

"THE Niagara season was over; the chatter of sight-seers had ceased, and the scene presented itself as one of holy seclusion and beauty. I went down to the river's edge, where the weird loneliness seemed to increase. The basin is enclosed by high and almost precipitous banks—covered, at the time, with russet woods. A kind of mystery attaches itself to gyrating water, due perhaps to the fact that we are to some extent ignorant of the direction of its force. It is said that, at certain points of the whirlpool, pine-trees are sucked down, to be ejected mysteriously elsewhere. The water is of the brightest emerald-green. The gorge through which it escapes is narrow, and the motion of the river swift though silent. The surface is steeply inclined, but it is perfectly unbroken. There are no lateral waves, no ripples with their breaking bubbles to raise a murmur, while the depth is here too great to allow the inequality of the bed to ruffle the surface. Nothing can be more beautiful than this sloping liquid mirror formed by the Niagara in sliding from the whirlpool.

"The green colour is, I think, correctly accounted for in the last Fragment. While crossing the Atlantic, in 1872—1873, I had frequent opportunities of testing the explanation there given. Looked properly down upon, there are portions of the ocean to which we should hardly ascribe a trace of blue; at the most, a mere hint of indigo reaches the eye. The water, indeed, is practically black, and this is an indication both of its depth and of its freedom from mechanically suspended matter. In small thicknesses water is sensibly transparent to all kinds of light; but, as the thickness increases the rays of low refrangibility are first absorbed, and after them the other rays. Where, therefore, the water is very deep and very pure, all the colours are absorbed, and such water ought to appear black, as no light is sent from its interior to the eye. The approximation of the Atlantic Ocean to this condition is an indication of its extreme purity.

"Throw a white pebble into such water; as it sinks it becomes greener, and before it disappears, it reaches a vivid blue-green. Break such a pebble into fragments, each of these will behave like the unbroken mass; grind the pebble to powder, every particle will yield its modicum of green; and if the particles be so fine as to remain suspended in the water, the scattered light will be a uniform green. Hence the greenness of shoal water. You go to bed with the black Atlantic around you. You rise in the morning, find it a vivid green, and correctly infer that you are crossing the bank of Newfoundland. Such water is found charged with fine matter in a state of mechanical suspension. The light from the bottom may sometimes cross, into play, but it is not necessary. A storm can render the water muddy, by rendering the particles too numerous and gross. Such a case occurred toward the close of my visit to Niagara. There had been rain and storm in the upper lake-regions, and the quantity of suspended matter brought down quite extinguished the fascinating green of the Horseshoe.

"Nothing can be more superb than the green of the Atlantic waves, when the circumstances are favourable to the exhibition of the colour. As long as a wave remains unbroken no colour appears; but when the foam just doubles over the crest, like an Alpine snow-cornice, under the cornice we often see a display of the most exquisite green. It is metallic in its brilliancy. But the foam is necessary to its production. The foam is first illuminated, and it scatters the light in all directions; the light which passes through the higher portion of the wave alone reaches the eye, and gives to that portion its matchless colour. The folding of the wave, producing as it does a series of longitudinal protuberances and furrows which act like cylindrical lenses, introduces variation in the intensity of the light and materially enhances its beauty."

The question of the colour of the Mediterranean and of other waters has been studied with a good deal of care by Aitken, whose work seems not to have received the attention which it deserves. Only a lengthy abstract of his paper is available and I quote from that. (Aitken, *Proc. Roy. Soc. Edin.*, 1882, xi., p. 472.)

"The experiments were made with a special view of determining whether the selective reflection or the selective absorption theory gave the correct explanation of the blueness seen in water. According to the selective reflection theory the colour is due to the light reflected by extremely small particles of matter suspended in the water, these particles being so small they can reflect only the short waves of light, or those which belong to the blue end of the spectrum. The other theory explains the colour by supposing that water has a selective absorption for the rays of the red end of the spectrum—that water is in fact a blue transparent medium. Three different methods were adopted of testing the correctness of these rival theories, and all three proved the water of the Mediterranean to be blue by selective absorption, and show that light in passing through the water has the rays of the red end of the spectrum absorbed, and only those of the blue end transmitted. The first method tried was to find out what is the colour of the illumination of submerged objects. This was done by taking a long metal tube, closed at the end with a glass plate, sinking it vertically in the water, and looking through it at white and different coloured objects fixed near the end of the tube. When this was done it was found that a white object appeared of a most beautiful deep and delicate blue at a depth of 6 m. If the selective reflec-

* From the *Journal of the Franklin Institute*, xxvii., No. 3.

tion theory was true, submerged objects would be illuminated with a colour complementary to that reflected by the fine particles, and would therefore appear orange or yellow, the exact colour depending on the amount of green in the reflected blue. If the blue colour of the sky, as generally supposed, is due to the reflection of the blue rays by small particles of matter suspended in the air, it obviously follows that light in passing through our atmosphere must become of a colour complementary to the blue of the sky; and it is asked, may this not be one of the reasons why the sun near the horizon, and all artificial lights, when seen at a great distance, appear more or less yellow?

"The second method of experimenting was by looking at a white surface through a considerable length of water contained in a blackened tube. The light transmitted was found to be blue, thus showing the water to have a selective absorption for the rays of the red end of the spectrum.

"The third method was by sinking white and different coloured surfaces under water, and noting the change which took place in the colours. The colours selected were red, yellow, and purple. It was found that these colours when seen through the water changed in the same way as when seen through a blue transparent medium, such as a piece of glass. The white changed to blue. The red darkened very rapidly as it descended, a very small depth of water being sufficient to destroy all the colour. At a depth of about 2 m. a very brilliant red was so darkened as to appear a dark brick red. Yellow changed to green by the water absorbing the red component of the yellow. An orange, as it sunk in the water, appeared to become more and more unripe, while a lemon became quite green. The purple surface quickly changed to a dark blue or violet by the selective absorption of the water. These changes, being all due to the cutting out of the red component of the colours, showed the water to have a selective absorption for the rays of the red end of the spectrum. If the water had been coloured blue by selective reflection, then those test colours would all have appeared deficient in blue when sunk in the water, as the fine particles would reflect and scatter the blue rays. Experiments are described which show that when these colours are sunk in water coloured blue by reflection from small particles, white changes to yellow, while yellow simply deepens in colour, and purple grows redder.

"All these different methods of experimenting show this water to be a blue transparent medium, and that it acts in the same way as a solution of a blue salt or as a blue tinted glass. It is then shown that this selective absorption theory is not enough to account for the different colour phenomena seen in water. A piece of blue glass or a blue solution have but little colour when viewed from the side on which the light is failing, and it seems certain that light will penetrate pure water till it is all absorbed, and the water will look dark and colourless. Something more, and that of great importance, is obviously necessary to explain the different colour phenomena seen in different waters, and in the same water at different times.

"If the water of the Mediterranean, when brilliantly coloured, is examined by means of a concentrated beam of light, it is found to be full of fine solid particles in suspension. It is shown that it is to this dust of the sea—so to speak—that the Mediterranean owes its fine and varied colouring. The particles of this aquatic dust are large, and reflect not only the blue rays, like the supposed particles of the selective reflection theory, but they reflect rays of all colours, and the water, by its selective absorption, strikes down the red rays, and only the blue rays are reflected to the surface and to the eye. These solid particles determine the brilliancy, and the selective absorption of the water determines its colour. The colour and the amount of the suspended particles is then considered. It is shown that the colour of the particles will have a marked influence in the appearance of the water. If the particles are yellow—sand particles, for instance—then a blue coloured water will appear to be green, as the light reflected by the yellow particles is deficient in the rays of the violet end of the spectrum.

"In the Mediterranean the solid particles are whitish, and all the different colour phenomena are easily explained by the different amounts of the reflecting particles at the different places. Where the colour is deep blue there are few particles in the water, and but little light reflected; and further, the light passes through a great amount of water, and undergoes a great amount of selective absorption before it is reflected to the surface and to the eye. But if there are many particles in the water much light is reflected, and the colour is chalky blue-green. as the light does not pass through so great a depth of water, and is therefore not so deeply coloured, nor has it so many of the green rays cut out as in the water where the particles are few and far separated.

"Colour experiments on a small scale with a solution of Prussian blue and a fine white powder are described. If the solution of Prussian blue is placed in a vessel, the bottom and sides of which are dark and reflect no light, then the coloured solution appears dark and colourless; but if a little of the white powder is added then the solution at once becomes brilliantly coloured. By varying the amount of the powder in the water all the varied colour effects of the Mediterranean can be reproduced, a little powder causing the solution to appear deep blue, and as more powder is added the brilliancy of the water increases, and its colour changes from blue to chalky blue-green.

"The presence and the abundance of white reflecting particles is shown to be a characteristic of all finely coloured waters, and the wave-washed shores of the Mediterranean are shown to be the factories in which are prepared its reflecting particles. The waves, as they beat on the shore, grind up the stones and rocks, and stir up a great amount of fine whitish solid matter, which gives the water along the shore a milky appearance.

"With the assistance of these whitish particles, we understand how it is that the brilliant blue-green of this sea depends so much on the continuance of sea-breezes. The longer the wave-mills have been at work the more fine powder has been produced along the shore, and more time given for the particles to be carried seaward, by the wave-mixed and wind-driven waters, and the blue-green which only extended in a narrow band along the shore, when the wind began to blow, is, after a few days of inshore wind, seen to extend far to sea. We also understand how it is that the colour near shore is so brilliant and so much greener than outside. Near the shore there is a greater quantity of white solid matter in suspension; there is therefore more light reflected, and further, the light does not penetrate through so great a depth of water, and has not so much of the light of the red end of the spectrum cut out, and therefore looks greener than the water outside, the light from which has to penetrate a greater depth of the absorbing medium. The blueness and beauty of the Mediterranean would thus appear to be due to the blue transparency of its waters, coupled with the presence of white reflecting particles, and the variety in its colouring to the amount of the suspended particles at different places and at different times.

"From this we see the important influence which the geological formation of the shore has on the appearance of the water of a sea, as it determines the nature of the solid suspended particles. This is beautifully illustrated by the difference of colouring in the Mediterranean at Mentone and at Cannes. At Mentone, limestone is everywhere abundant along the shore, and this limestone, when ground up by the waves, produces an extremely fine and white powder, which mixed with the water, causes the sea at Mentone to be far more brilliantly coloured than it is at Cannes, where there is but little limestone, and the shore is almost everywhere covered with sand, the débris of the surrounding rocks.

"In the experiments in the Mediterranean it was found that the solid particles were so abundant that they pre

vented the sun's rays penetrating in a direct line to any great depth. This was shown by the illumination of the white surface placed at some distance under the water, and seen through the empty tubes, being the same, whether the surface was turned towards the sun or away from it. It was also shown by the fact that at a depth of 6 m. these solid particles were found to reflect about as much light as a white surface did. These solid particles act like a fog, and, while they stop the light penetrating in a direct line, yet allow it to penetrate much further by internal reflection. The sun's rays get entangled —so to speak—among the particles, and are reflected from particle to particle, becoming a deeper blue with each reflection so that the particles become illuminated with blue light. From this it is obvious that the more transparent the water, and the greater the reflecting power of the particles, the more deeply coloured will the water appear.

"The Lake of Como was the next water visited. A white surface seen through its waters showed it to be as deeply coloured as the Mediterranean, yet the absence of white reflecting particles in its waters and its dark-coloured bottom, cause it to appear comparatively dark and colourless. When a quantity of white reflecting particles are artificially mixed up with the water in this lake a fine blue-green cloud was formed, which remained visible for some time amidst the darker waters, and showed that all this lake required to make it brilliantly coloured was the presence of white suspended particles in its waters. The waters of Como, in their passage from the lake to form the river Adda, change to a fine blue. This sudden alteration in the appearance of the water is shown to be probably due to the addition of fine reflecting particles to the water on entering the river. Lago Maggiore, compared with Como and the Mediterranean, looks greener than either, but reflects more light than Como.

"The Lake of Geneva, whose waters have been so highly praised by all writers, was next visited, and the explanation given of the colouring of the Mediterranean was found to apply here also. Near Bouveret, where the Rhone enters the lake, all the variety of colour phenomena seen in the Mediterranean were repeated. The light coloured muddy waters of the entering river, as they stretched far into the lake, represented the whitish waters near shore in the Mediterranean, and where this whitish stream mixed with the waters of the lake, the bright blue-green of the Mediterranean was reproduced, while further out the waters were deeper blue, rivalling in brilliancy those of the Mediterranean. The work done by the waves along the shores of the Mediterranean in manufacturing the light reflecting particles, is for the lake of Geneva, done by the grinding of the glacier mills and streams of the Rhone valley.

"The silt brought down by the Rhone was found to be composed of clean white particles, like fine white sand. Many of the particles are thin polished plates, and when examined by means of a concentrated beam of light, while in suspension in water, are seen to flash brilliantly in the strong light. This white solid matter brought down by the Rhone is constantly being deposited all over the bottom of the lake, and it is this whitish deposit which gives to the Lake of Geneva one of its peculiarities. The light reflected from the whitish bottom causes the water of the lake, all along the shore, to appear of a peculiar light blue green colour, and enables us to judge of the depth of the lake at depths far beyond that to which we can see the bottom. We can only see a white surface of 15 cm. square to a depth of about 7 m., yet the light reflected from the bottom affects the appearance of the water at depths far beyond 7 m., showing that light penetrates by diffusion in these waters to far greater depths than it can directly. The brilliancy and beauty of the Lake of Geneva would thus appear to be due to the purity and transparency of its waters, coupled with the presence of an enormous amount of white reflecting surfaces, both in suspension in its water and deposited all over the bottom of the lake, the effect being intensified by the brilliancy of the reflecting particles.

"The colour of the water in Lake Bourget was found to be similar to that in the Lake of Geneva, though at the time it was visited it was slightly more turbid. A white surface could not be seen to so great a depth as in Geneva, and the water, even in the middle of the lake, when examined by means of a concentrated beam of sunlight was found to be very full of suspended light-reflecting particles similar to those brought down by the Rhone. The examination of the water in these lakes was confined to the coloured surface experiments, and to a spectroscopic examination of the internally reflected light. The results were all similar to those in the Mediterranean.

"In the beginning of autumn the sea off the west coast of Scotland, near the village of Ballantrae, and also in Brodick Bay, was visited, and the water examined by means of submerged coloured surfaces, and by means of the spectroscope. The water was here found to be much greener than any previously examined. A large quantity of this water was filtered, when it was found that most of the suspended particles were fine grains of sand. From this it is concluded that the greenness of our northern seas is in part due to the reflecting particles being yellow, and the reflected light, therefore, deficient in the more refrangible rays. These yellow sand particles not only explain part of the greenness of our northern seas, but they also explain their comparative darkness and deadness, the yellow sand particles reflecting so little light. The importance, however, of even these bad reflectors was very evident during the time the observations were being made. It was noticed that the water was much more brilliantly green during and immediately after an inshore wind, and when the filter showed the water to have a good deal of sand in suspension, than after a calm, when many of the particles had settled out. Some water collected about a mile seaward from Ballantrae was examined in a glass tube 7½ m. long, and was found to be of a blue-green colour.

"The water of Loch Lomond was next examined, and found to be a perfect contrast to any previously described, being of a colour nearly complementary to that of the Lake of Geneva. A white surface seen through its waters appeared yellow, and the submerged coloured surfaces showed its waters to have their greatest absorption for the rays of the violet end of the spectrum. Its waters reflect a slightly yellowish light, its spectrum being brightest in the yellow. This water is so deficient in reflecting particles that its brightness is never greater than what we call brown. If it was supplied with abundant reflecting particles Loch Lomond would be a yellow lake.

"Well waters were also examined for colour by placing them in long tubes, and looking through the water at white and at coloured surfaces. The tubes were in pieces, so that they could be fitted up in lengths of 3 m. to 15 m., to suit the transparency of the water under examination. The tubes were fixed horizontally, and at a convenient height for looking through them, and the water to be tested was poured in till the tube was half full, so that by looking through the upper half of the tube the coloured surface could be seen, and through the lower half the effect of the absorption of the water on the colour, and on the brilliancy, of the transmitted light. The transmitted light was also examined by means of a spectroscope.

"The colours of the different waters were found to vary greatly. One sample was of a fine blue, others were green-blue, some green, whilst others were of colours between green and yellow, but all were of colours between blue and yellow. It was observed that the more transparent a water was, the nearer its colour was to blue. Scarcely any light could be seen through 7 m. of any of the yellowish waters, whilst through this length all the bluish waters were quite transparent, and the spectroscope showed that some of the waters transmitted almost the entire light of the blue end of the spectrum, and only stopped the rays at the red end. When one of the bluish

waters was examined in a tube 15 m., or nearly 50 feet long, it appeared of a fine blue-green as transparent as a piece of glass.

"Only a very little relation could be traced between the colour of a water—*when tested in long tubes*—and its suitability for dietetic purposes.

"The *cause* of the colour of water has been a frequent subject of speculation. Every substance which has been discovered in water has in turn been suggested as the cause of the colour. When no useful purpose could be given for its presence, it was told off to do the ornamental, and make the water beautiful to the eye. All these speculations assume that the colour is due to some impurity in the water. This, however, is obviously begging the question. It is first necessary to find out whether water has any colour in itself, and what that colour is, before we can say anything about the effect of impurities. As it would be impossible to prepare absolutely pure water, and as we might still be in doubt as to whether any colour seen in purified water was due to the water or to the impurities, the following method of experimenting was adopted: Distilled water was prepared in two sets of apparatus; in one set the condensing tube, the collecting bottle, and the testing tube were all of glass; in the other set they were all made of brass. If the waters prepared in these two sets of apparatus have the same colour, then the probability is that the colour is due to the water, as the impurities will be different in the two samples, and they would probably give different colours. The result was, the colour of the samples of water prepared in both sets of apparatus was the same—namely, blue. This conclusion was further confirmed by preparing another sample of the water, and condensing it this time in a platinum tube. The water so prepared was also found to be of a fine blue. All three samples were almost exactly the same colour as Prussian blue. Standards of colour were kept, with which the different samples of water were compared, both for the colour and for the amount of the colour. As all the different samples of distilled water—after the apparatus was thoroughly purified—had the same colour and amount of colour, it seems almost certain that water is a blue transparent substance, and that the colour in these experiments could not be due to impurities, which must have varied both in kind and in amount in the different samples of water. Further, as the amount of colour in the Mediterranean water, and in the bluish well waters was, as near as could be judged, the same as in pure waters, it does not seem necessary to call in the aid of impurities to account for the blue colour seen in the lakes and seas, the colour being principally due to the water itself, and the different substances in solution, instead of making the water blue, tend to change its proper colour and make it green or yellow.

"The addition of impurities to water seems generally to change its colour from blue to green, or to yellow, though there seems to be no reason why some impurity may not change it to a deeper blue. The selective-absorption of the water remains the same, while the impurities add their selective-absorption to that of the water, and while they change the colour they also decrease its transparency. This explains why it is that the yellow well waters are so much less transparent than the blue. This must necessarily be so, as a very small depth of water destroys the rays which give yellow, and the transparency of yellow waters can only be the transparency of water for yellow light, which is very much less than for blue light. No attempt was made to find out what the different discolouring substances in water are. The task would evidently be an endless one, and of little value.

"The effect of the light reflected from the surface of the water is then referred to. It is shown that when the sky is covered with white clouds, the surface reflection is so strong as to mask the colour of the water, and that when the sky is deep blue the sky-reflected light intensifies and deepens the apparent colour of the water. The importance of the surface-reflected light is best seen when the sky is covered with clouds, and glowing with a colour different from that of the water, as at sunset when the clouds are richly coloured all over the sky and deeply down towards the horizon. The water will then, especially if calm, appear like a sea of molten metal glowing with sky-reflected light, so powerful and brilliant as entirely to overpower the light internally reflected by the water.

"Pure water having been shown to be perfectly transparent to the more refrangible rays, and as it absorbs the red rays, water, when looked at from the side on which the light is falling, must necessarily be dark, and cannot reflect any perceptible amount of blue light. We must therefore look to the solid particles in suspension in the water as the cause of the light reflected by water, and while the selective absorption of the water principally determines its colour, its brilliancy is entirely determined by the suspended particles. It is shown why it is that though we have waters of many colours, yet we only observe the colour when it is blue or green, and never when it is yellow. Amongst other reasons given is the much less brilliancy of yellow waters, this less brilliancy being due to the less transparency of the yellow waters compared to blue; only the reflecting particles near the surface are active in the yellow water, whereas the particles to a considerable depth in the blue can reflect their light to the surface. This is one reason why Loch Lomond is so much darker than the Lake of Geneva. Loch Lomond certainly has fewer and less powerful reflecting particles than the Lake of Geneva, but it is darker also, because only the particles to a much less depth can reflect their light to the surface.

"The waters of our northern seas, when provided with proper reflecting particles, such as air-bells and white particles, are shown to be much bluer than they generally appear. The brightness and blueness of the waters off the coast of Cornwall are shown to be due to the beaches along this coast being at many points covered with a whitish-coloured sand, which gets mixed up with the water by the action of the waves. As the water of the sea is constantly circulating, it seems impossible that the same water can be one colour at one place and a different colour at another, but we can easily see how the different colours and degrees of brilliancy can be produced by the colour and the amount of suspended matter at the different places—where the water is mixed with whitish particles being bluish, and where mixed with yellow particles appearing greener—whilst its brilliancy is determined by the amount of suspended particles which may be present at the time in the water.

"In conclusion, a lake in the Cordilleras is referred to as combining all the conditions necessary for producing fine and brilliantly blue coloured waters. The traveller in describing this lake says: 'Its waters were of the most extraordinarily brilliant blue I ever beheld.' From the description, this lake is in many respects like the Lake of Geneva. It is provided with an abundant supply of pure glacier water, free from discolouring impurities, but laden with abundance of white-reflecting particles, whose presence is evidenced by a 'white strip' around the lake."

In a letter to Prof. Tait, dated Mentone, April 14, 1882, Aitken (*Proc. Roy. Soc. Edin.*, 1882, xi., 472) says:—

"Since coming here this time I have tested the sea with the polariscope and with the spectroscope. With an instrument by Hoffman, which gives coloured bands with polarised light, I have been able to detect small, but decided indications of polarisation in the light internally reflected by the water, the surface reflection being, of course, cut off when the observation was made. At present I think the polarisation is due to regular reflection from the polished surfaces of some of the particles, which are seen to glance brightly in concentrated sunlight.

"I have also detected an absorption band in the green of the spectrum of the light internally reflected by the Mediterranean water. This band is much more distinct in water where there are but few reflecting particles, and the light undergoes a great amount of selective absorption.

At about a mile from shore, where I could see a white surface 6 inches square at a depth of 16 metres, the absorption band was quite distinct, but became less and less as I approached the shore, where there was more matter in suspension and the water less transparent, but the spectrum more brilliant. I cannot say whether this band belongs to water or to salt, or to what it is due, never having noticed it before; but I never examined water so transparent, and where the light had undergone so much absorption."

Subsequently to Aitken, but apparently independently, Spring (*Bull. Acad. Roy. Belg.*, (3) 1883, v., 55) made a thorough and interesting study of the colour of water. "Water in large masses always appeared coloured to us; but the colour is not always the same and the tints are rich and vary enormously. The Mediterranean is the most beautiful indigo; the Atlantic is sky blue; the Lake of Geneva is famous for the beauty of transparency of its azure waters; the Lake of Constance, the Rhine which flows from it, the Lake of Zürich, and the Lake of Lucerne are just as transparent, but the waters are more green than blue. The little Kloenthaler Sea near Glaris can scarcely be distinguished from the surrounding fields, the water is so near the colour of the grass on the banks. Among the more deeply coloured waters I will mention only the Lake of Staffel near Murnau at the foot of the Bavarian Alps. On the day that I saw it, the water seemed absolutely black, although perfectly clear when seen in thin layers.

(To be continued).

A CONTRIBUTION TO THE CHEMISTRY OF TELLURIUM SULPHIDE.*

By AARON M. HAGEMAN.

A CAREFUL study of any compounds which tellurium is able to form with sulphur is of special interest to the inorganic chemist from a twofold view-point. First, it may serve more definitely to establish the true chemical character of tellurium, and second, it may furnish positive information regarding the possible complexity of that element whose atomic weight has already been more exhaustively studied than any other element known to chemists.

Although Berzelius (*Pogg. Ann.*, 1826, viii., 411) in 1826, reported that two sulphides of tellurium could be prepared by passing hydrogen sulphide gas into acidified aqueous solutions of tetravalent and hexavalent tellurium, respectively, Becker (*Ann.*, 1876, clxxx., 257) showed that the resulting precipitates were not true chemical compounds, since a large part of the sulphur could be extracted with carbon disulphide. The existence of true sulphides of tellurium was therefore questioned.

However, Becker was unable to remove completely all the sulphur from these precipitates by carbon disulphide. He states that a minimum of 3·69 per cent of sulphur is always retained by the tellurium. This phenomenon has attracted the attention of chemists, who have seen a clue to the suspected complexity of tellurium, since the unidentified hypothetical impurity in tellurium must have a higher atomic weight than tellurium, and consequently ought to form a more stable sulphide.

Such has been the assumption of Brauner (*Monats.*, 1889, 456), of Gutbier and Flury (*Zeit. Anorg. Chem.*, 1902, xxxii., 272), and of others.

However, none of these workers has been able to obtain positive evidence of the existence of any compound between these two elements, while all attempts to remove completely the sulphur from the precipitate have failed, though Gutbier and Flury have succeeded in reducing the amount of sulphur retained by the tellurium from 3·69 per cent as reported by Becker to 1·19 per cent.

Snelling (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 802) more recently has reported the isolation of an unstable compound of tellurium and sulphur having the formula TeS. He obtained this compound by passing hydrogen sulphide into an acid solution of tellurous acid of known strength at 0° C. After passing in the gas for twenty minutes, 30 cc. of carbon disulphide which had also been cooled to 0° C. was added and allowed to stand in contact with the precipitate for twenty minutes. The undissolved portion was collected on a filter and analysed. His analysis showed tellurium and sulphur approximately in the ratio required by the compound TeS. Consequently he has stated that at the moment of precipitation one-half of the sulphur is chemically combined with the tellurium as TeS while an equal amount of sulphur exists in the precipitate as free sulphur. He further states that the compound TeS is unstable, decomposing at 0° C. in about four hours, or instantly if heated.

The work about to be described was undertaken in the hope of throwing some light upon the chemical condition of this small amount of sulphur which resists the action carbon disulphide, and to investigate further any true chemical union which may exist between tetravalent tellurium and sulphur. The latter problem was attacked by first carefully repeating Snelling's (*loc. cit.*) experiments in aqueous solution and then carrying out the precipitation of tellurium sulphide in non-aqueous solutions in order to determine whether the medium had any effect upon the composition and stability of the precipitate produced.

Materials.

Tellurous Acid.—Crude tellurium containing, as its principal impurities, small amounts of copper and selenium, was oxidised with aqua regia. The tellurium dioxide thus obtained was freed from nitric acid by gentle ignition, dissolved in concentrated hydrochloric acid, its solution diluted with an equal volume of water, and filtered. From this solution selenium and tellurium were precipitated by sulphur dioxide. After washing with water until free from chlorides, they were fused with KCN at a dull red heat with the formation of potassium selenocyanate and potassium telluride. The fusion product was dissolved in hot water and the tellurium precipitated by means of a current of air, the selenium remaining in solution. This gave very pure tellurium.

This tellurium was dissolved in nitric acid and crystallised twice from dilute nitric acid as the basic nitrate. This was ignited and fused to the dioxide, which, on cooling, crystallised in long, pale yellow crystals. On grinding, a white powder resulted which yielded, upon analysis, by the method of Lenher and Homberger (*Journ. Am. Chem. Soc.*, 1908, xxx., 378), 80·06 per cent Te. Calculated 79·99 per cent. (The figure 127·6 has been used for the atomic weight of tellurium). Tellurium dioxide was converted into tellurous acid by dissolving in hydrochloric acid and diluting the solution with water to the strength desired.

Hydrogen Sulphide.—This gas was made by the action of hydrochloric acid on sodium sulphide. It was washed with sodium sulphide solution and dried with calcium chloride before being used.

Carbon Disulphide.—The carbon disulphide used in the investigation was freed from sulphur by allowing it to stand over copper turnings for at least two weeks. It was then filtered away from any black particles of CuS which had separated and was distilled, only those portions being saved that came over between 44° C. and 48° C. This product left no residue of sulphur on spontaneous evaporation. It was purified as used, no attempt being made to keep the purified product.

Experimental.

A solution of tellurous acid containing 5 per cent free hydrochloric acid was prepared and its exact tellurium

* Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xli., No. 3.

content determined by the Lenher-Homberger (*loc. cit.*) method.

Three samples were taken from this solution and placed in 300 cc. Erlenmeyer flasks. Concentrated hydrochloric acid was added till the samples contained 20 per cent, 10 per cent, and 5 per cent hydrochloric acid. These solutions were placed in a thermostat carefully regulated at 25° C., and after they had attained that temperature, were treated with pure, dry hydrogen sulphide gas until precipitation was complete. In all cases the hydrogen sulphide caused the immediate formation of a dark red voluminous precipitate which increased in volume until most of the tellurium had precipitated, when it began to coagulate in small granules. Simultaneously with this decrease in volume, the colour gradually became darker until the tellurium had quantitatively precipitated as a black mass which settled to the bottom of the flasks. The precipitates were brought upon tared Gooch filters, washed with water containing hydrogen sulphide gas, followed by hot water, then dried in a vacuum over phosphorus pentoxide at room temperature, and weighed. The results obtained follow:—

	Grm.
Weight of Te and S required for TeS_2	0·3035
Weight of Te and S found (20 p.c. HCl)	0·3031
Weight of Te and S found (10 p.c. HCl)	0·3034
Weight of Te and S found (5 p.c. HCl)	0·3038

These results establish two definite facts—First, the precipitate obtained by the action of hydrogen sulphide gas on acid solutions of tetravalent tellurium contains tellurium and sulphur in the ratio 1 : 2; and second, that the concentration of acid has no effect upon this ratio.

The Extraction of Sulphur from the Precipitate.—A precipitate obtained as above from a sample of tellurous acid containing about 5 grms. of Te was transferred to an extraction thimble and extracted in a Soxhlet extractor with carbon disulphide for twelve hours. Then it was freed of carbon disulphide by carefully washing with alcohol, followed by ether, and a sample was analysed for its sulphur content. This was accomplished by treating with nitric acid followed by fuming nitric acid in the cold until oxidation was complete. The solution was evaporated to dryness, the residue taken up in 8 per cent hydrochloric acid, and the sulphur determined by the usual gravimetric method.

The results showed 1·36 per cent and 1·34 per cent sulphur retained by the tellurium, in fair agreement with the results obtained by Gutbier and Flury (*loc. cit.*). By a longer extraction with carbon disulphide these investigators were able to reduce this figure to 1·19 per cent. The experiment shows, however, that a carbon disulphide extraction of comparatively short duration will remove readily all but 1·35 per cent of the sulphur.

Since, then, a small part of the sulphur does not dissolve in carbon disulphide, we may assume three possibilities regarding the chemical condition of this small percentage of sulphur. It may exist in the precipitate in chemical combination with the tellurium or, perhaps, with some undiscovered element more metallic in nature. Such an element would undoubtedly form a sulphide which would completely resist the action of carbon disulphide. Then, again, this sulphur may exist as a form of elementary sulphur that is insoluble in carbon disulphide, though no one appears to have considered this possibility.

To test the two first possibilities, the following experiment was carried out:—A large sample of completely extracted material was treated in a large test-tube with 1 to 1 hydrochloric acid and water and gradually warmed. The test-tube was fitted with a one-holed rubber stopper, and the gases which came off were directed against a filter paper saturated with a solution of lead acetate containing a large excess of sodium hydroxide. Not the faintest coloration which would indicate hydrogen sulphide could be obtained. The experiment was repeated, using stronger hydrochloric acid and also hydrobromic acid of various strengths, but with negative results. Although these experiments do not prove conclusively that no sulphide exists in the precipitate, it shows that no sulphide which either hydrochloric or hydrobromic acid is capable of decomposing exists in the precipitate.

Amorphous sulphur is known to chemists in one form which is soluble and one which is insoluble in carbon disulphide. The insoluble amorphous modification, frequently known as gamma sulphur, can be produced by decomposing sulphur monochloride with water or by the interaction of hydrogen sulphide and sulphur dioxide. It would not be surprising, therefore, if the latter variety of sulphur were formed here in the decomposition of the tellurium-sulphur precipitate.

The insoluble variety of sulphur may be converted into soluble sulphur by long boiling with alcohol or by subjecting it to a pressure of 8000 atmospheres. The latter method being impractical, the former was resorted to.

The conversion was attempted in the following manner:—A large sample of tellurium sulphur was precipitated as usual and most of the sulphur extracted in a Soxhlet extractor with carbon disulphide. Then the carbon disulphide was removed carefully and the extraction continued with absolute alcohol. By this means the precipitate was subjected to the action of hot alcohol and, at the same time sulphur was dissolved away as rapidly as it was converted to a soluble form. At the end of twenty-four hours of continued extraction, the alcohol had assumed a yellow colour, indicating that some sulphur had been removed from the precipitate. On dilution with water an opalescence confirmed the presence of a small amount of sulphur. The alcohol in the flask was replaced with fresh alcohol and the extraction continued. At the end of the second day the alcohol again became slightly opalescent upon dilution with water. This process was continued for nine days, the used alcohol being replaced with fresh alcohol each day. At the end of this period, since the alcohol showed no trace of opalescence upon dilution with water, a sample was removed and analysed for sulphur. The analysis showed 0·95 per cent and 0·96 per cent of sulphur present in the precipitate. Consequently the extraction was continued for one month. Samples were again removed and the sulphur determined; 0·93 per cent and 0·96 per cent of sulphur still proved to be present in the precipitate.

From these results it is evident that this small amount of sulphur does not exist in the free state, or, if so, in an extremely insoluble and inert form. The manner in which this sulphur exists chemically remains an unsolved problem.

The Non-existence of TeS.—The work of Snelling (*loc. cit.*) at 0° C. has been repeated in detail with only those changes found necessary to increase the accuracy of the results obtained. A sample representing 0·2020 grm. of elementary tellurium was used. The solution was carefully cooled to 0° C. by means of an intimate mixture of pulverised ice and water. The hydrogen sulphide, after being freed from hydrochloric acid gas and dried, was passed through a long coil condenser similarly cooled. After passing the gas into the sample for twenty minutes, 60 cc. of purified carbon disulphide cooled to 0° was added. By a whirling motion the precipitate was completely forced into the carbon disulphide which occupied the bottom of the flask in which the precipitation was made. After standing in the freezing mixture for fifteen minutes, the carbon disulphide assumed a yellow colour and the precipitate became black and granular. The contents of the flask were brought upon a tared Gooch filter which had also been cooled to 0° C. The precipitate was washed with water and dried *in vacuo* over P_2O_5.

Te in sample, 0·2020 grm.; required for TeS_2, 0·3035; required for TeS, 0·2527 grm.; weights of Te and S found, 0·2540, 0·2537, and 0·2542 grm.

These results were of special interest since the weights of tellurium and sulphur found were always slightly higher

than the weights required for TeS and considerably lower than those required for TeS_2. A number of such determinations were made, and all tended to show that a compound containing more sulphur than TeS was at first produced.

Assuming that TeS_2 might be produced at first, a series of experiments was carried out in which the time elapsing between the first introduction of hydrogen sulphide gas into the solution and the final removal of the precipitate from the carbon disulphide was reduced from thirty-five to ten minutes. These results seemed desirable since the rapid change in colour taking place immediately after precipitation might indicate the gradual dissociation of the product first formed into its elements. Hydrogen sulphide was passed in for five minutes and the resulting precipitate extracted with carbon disulphide for five minutes.

The results obtained furnished further evidence that TeS was not formed primarily. However, it was difficult to obtain uniform results, and it appeared that all the factors had not been taken into account. The two chief uncertainties were, whether the tellurium was completely precipitated in this length of time and whether the carbon disulphide was in contact with the precipitate a sufficient length of time to remove all free sulphur.

A qualitative test of the filtrate showed small amounts of tellurium still remaining in solution, indicating incomplate precipitation. In order to determine the exact amount of tellurium in each case the Gooch crucibles containing the completely dissociated precipitates were extracted with carbon disulphide until they failed to lose weight. Since all but 1·35 per cent sulphur could be removed, the weight of tellurium in the precipitate was easily calculated.

The use of this method made it necessary to determine whether tellurium itself was entirely insoluble in carbon disulphide. A series of extractions of precipitated tellurium with carbon disulphide in a manner exactly similar to the extractions given the tellurium-sulphate precipitate proved this to be the case. Consequently a series of experiments was carried out using carbon disulphide as the extraction agent. The exact weight of tellurium precipitated in each case was calculated from the weight of the completely extracted precipitate. The precipitates were allowed to stand in contact with the precipitate for exactly five minutes. The results of the experiments are given in the following table:—

Wt. of Te. Grm.	Required for TeS. Grm.	Required for TeS_2. Grm.	Wt. of TeS ppt. Grm.	S in Te S ppt. Per cent.
0·1956	0·2931	0·2447	0·2884	32·18
0·1968	0·2957	0·2462	0·2891	31·93
0·1990	0·2990	0·2490	0·2943	32·34

Besides explaining why it was impossible to obtain uniform results in the previous experiments, these results furnish more complete evidence that the original precipitate could not have had the composition TeS.

In order to determine whether five minutes was sufficient time for all separated sulphur to be taken up by the carbon disulphide, the following experiment was carried out:— Since hydrogen sulphide has no action on carbon disulphide it was found possible to have carbon disulphide present during the precipitation. This provided for a ten-minute extraction of the greater part of the precipitate. Results of such experiments follow:—

Wt. of Te. Grm.	Required for TeS_2. Grm.	Required for TeS. Grm.	Wt. of TeS ppt. Grm.	S in Te-S ppt. Per cent
0·1858	0·2792	0·2334	0·2733	32·02
0·1879	0·2823	0·2351	0·2751	31·70
0·1932	0·2903	0·2417	0·2855	32·32

These results showed that five minutes was adequate for the removal of all free sulphur, since these results were in close agreement with those obtained by the five-minute extractions. Moreover, they appear to warrant the conclusion that the first product produced by the action of hydrogen sulphide upon aqueous tellurous acid solutions is not a compound represented by the formula TeS but must be a compound containing a greater amount of sulphur.

One phase of the methods employed up to this point was not entirely satisfactory, namely, the use of a numerical constant in determining the actual weight of tellurium precipitated. An apparatus was consequently devised which permitted a gravimetric determination of the tellurium precipitated, thereby giving a direct instead of an indirect method for the determination.

(To be continued).

PROCEEDINGS OF SOCIETIES.

SOCIETY OF GLASS TECHNOLOGY.

The Annual Meeting of the above Society was held on Wednesday, April 16, in the Applied Science Department of the University of Sheffield. Mr. W. F. J. Wood, C.B.E., President, took the chair.

After the annual report of the Society had been read, the Officers for the coming year were elected, Mr. S. N. Jenkinson, M.B.E., becoming the Society's new President.

After the formal business had been dealt with, Mr. Wood gave a short presidential address, in which he spoke of the Research Association that had been formed in the glass industry. A provisional committee had been appointed, and at an early date all manufacturers in the Industry would be invited to join the Glass Research Association. Substantial promises had already been received, and it was felt that the scheme would be a great success, especially as it was being looked upon with such favour by the Department of Scientific and Industrial Research.

Mr. A. P. M. Fleming, O.B.E., Director of Education and Research for the British Westinghouse Co., gave a most interesting and instructive account of Industrial Research in the United States.

Sir Frank Heath, Secretary of the Government Department of Scientific and Industrial Research, then addressed the meeting. He pointed out the glass industry had been engaging the anxious consideration of the Government as much, if not more, than any industry in the country since the war began. During the war the Department had been enabled to help the Industry in many ways, and would do so in the future. There was considerable research still to be carried out, but this would cost money, and take time. He could not help feeling that too much dependence upon state aid indicated an unhealthy condition in industry. It ought not to be necessary for any industry to look outside itself for direct and immediate aid in the conduct of its work. That was not the past of British Industry, which was where it is by its own efforts, a fact we were very proud of. It was certain that British Industry would have to save itself by organisation, and work from within. There was very great call from other industries besides that of glass for State Aid in Research. Research was insurance for knowledge, and he appealed to the Research Association to get the best men possible for their work, and then they would be absolutely certain of good results.

Dr. W. E. S. Turner addressed the meeting. He emphasised the need for research, and showed how it would advantage small firms as well as the great. He gave several examples where money had been wasted and was being wasted for lack of scientific knowledge and supervision. The chemist in co-operation with the engineer was a safeguard in the industry, and he appealed for researches in glass on the pure side as well as the applied.

Before the meeting the Department of Glass Technology was thrown open to members of the Society, many interesting and instructive operations being carried out. Mr. J. B. Davidson, M.Sc., F.I.C., showed the casting of a 2 cwt. Glass Pot.

After the visit of inspection, members of the Society had the valuable opportunity of seeing the Vacuum Casting of a large Glass Pot. The pot when finished was some 38″ in diameter, and of the hooded variety. The demonstration was carried out by Mr. B. J. Allen.

In the evening the Society held their first annual dinner in the Grand Hotel; the chief guest was the past President, Mr. W. F. J. Wood, C.B.E., B.Sc. The other guests present included Dr. Ripper (Vice-Chancellor of Sheffield University), Sir Frank Heath, Dr. F. E. Bradley, Mr. A. P. Trotter, Mr. W. Gibbons, Mr. P. V. B. Tippetts, Mr. A. P. M. Fleming, Mr. T. Mortimer Sparks (Commercial Editor of the *Sheffield Daily Telegraph*), Mr. R. Ainger (Commercial Editor of the *Sheffield Independent*).

The next meeting of the Society will be held in London on May 21, when it is hoped that Dr. Walter Rosenhain, F.R.S., will read a paper on "Refractories Research" carried out at the National Physical Laboratory. On the morning of the meeting members will be given the opportunity to visit the National Physical Laboratory.

NOTES.

OSMOTIC PRESSURE AND PREPARED FOODS. – In keeping preserved foods enclosed in skin, osmotic pressure on the membrane of even slightly salt solutions will tend to prevention of putrefaction. An attending phenomena that such is the case is that during sudden fall of temperature there is a distinct exudation of water.—J. C. THOMLINSON, B.Sc.

OSMOSIS AND EMULSIONS.—Osmotic pressure in the presence of emulsions in organic semi-solutions and in pastes gives rise to phenomena, two of which may be described. In the first, solutions of a colloidal character evaporated *in vacuo* may, after standing for some time, contract to a considerable extent, in which neither contraction on cooling or normal evaporation can be advanced as the immediate causes. In the second, organic pastes contained in membranes, on cooling the external surroundings, transfuse water by osmosis in quantity, the liquid exuded bearing a considerable ratio to the paste left.—J. C. THOMLINSON, B.Sc.

A NEW Association called the Technical Inspection Association has recently been formed, which should appeal very strongly to many technical men throughout the Empire who are in any way interested in inspection work. It is the outcome of the Ministry of Munitions Inspection Department, and has been formed for two main purposes:—(1). To maintain intercourse and promote mutual assistance among its members. (2). To conserve and co-ordinate for the national use the experience brought together by the War and generally to develop the progress and standardisation of inspection in the engineering, chemical, and allied industries. Owing to the stoppage of war work the services of large numbers of men, most of whom possess high technical qualifications, and who have spent several years on the inspection of Government contracts, are now available. A list of such members is held y the honorary secretaries, who will be glad to supply particulars to any who may be interested.

THE Hardware and Engineering Supplies Co., Ltd., 16, Water Lane, Great Tower Street, E.C. 3, are manufacturing amber glues in liquid and jelly form, as used by ply wood manufacturers, aircraft and cabinet manufacturers, box makers, and bookbinders, superstarch for launderers in liquid form, and soft soaps and soap bases, and desire publications bearing on these industries.

FREDERICK COPE, Consulting Engineer, Southgate Chambers, Wakefield, desires information re the most efficient plant and up-to-date methods in connection with brickmaking. Also the most modern process for rag carbonising.

THE Board of Trade announce that the Fuel Order, 1918, which controls the sale of wood for fuel, will cease to have effect as from April 30.

IT is notified that Messrs. F. Bunn, King's Lynn, G. V. Sedgwick, Middlesex, and B. C. Wilkinson, Reigate, nominated under the 8th Section of the Weights and Measures Act, 1904, have passed the examination provided for under that Section.

A CONSIDERABLE number of merchants and business representatives who formerly lived in Russia are at the present time in the United Kingdom owing to the actions of the Bolsheviks. As a considerable part of the former Russian Empire is now available for trade, it may be that firms in this country would be glad to take advantage of the present exceptional opportunity of obtaining the services of these men, who are especially well qualified to open up trade with Russia. The Department of Overseas Trade would be glad to hear from any firm that desires to be brought into touch with the persons referred to, either immediately or later on, when trading in a more general way can be conducted with Russia. Enquiries should be addressed to the Russian and Scandinavian Section, Sunderland House, Curzon Street, Mayfair, W. 1.

AMONGST the questions which the closing months of the war have brought to everyone's notice there is none of wider interest than domestic service. For although it is the custom to joke over "the servant problem," it comes home vividly to every man and woman in the kingdom. Scoffers may laugh at including elementary science in a cook's training, but how else is she to understand and remember why cold water removes the smell of onions while hot water fixes it; why certain foods should be put down in boiling water while others need cold water; why the contents of some saucepans are to be kept covered and others not? In every department of work the more thoroughly you understand the reason for your routine actions the more interesting they become. For that reason it is always well, where possible, to follow up orders with a brief reason for them—it also fixes the order in the maid's memory and prevents her thinking in some cases that it is purely arbitrary, if it seems at first sight slightly more troublesome than her old method.

NOTES FROM FOREIGN SOURCES.

Yellow Cuprous Oxide.—L. Moser. – The best way to prepare yellow cuprous oxide is by the reduction of Cu″ ions in presence of OH′ ions by means of hydroxylamine hydrochloride, and the electrolytic method, using a pure copper anode and alkali sulphate as electrolyte. The light yellow product which is first precipitated is very probably cuprous hydroxide, which spontaneously gives up water at a low temperature and is converted into the reddish yellow hydrated cuprous oxide which is amorphous. The dry yellow cuprous oxide is quite stable in air, but it shows a tendency to pass very slowly into the crystalline form. This very slow process can be hastened by heating the amorphous product in absence of air. The yellow cuprous oxide must thus be regarded as the primary metastable form which shows a tendency to pass into the metastable red crystalline modification.—*Zeit. Anorg. Chemie*, 1919, cv., 112.

A very Sensitive Reaction of Copper. Application to the Analysis of Ash and Arable Soils.—L. Maquenne and E. Demoussy.—When a hydrochloric acid solution of an ash, sufficiently concentrated and carefully freed from iron and manganese, is treated with potassium

ferrocyanide, ordinarily the liquid assumes a yellowish pink tint, indicating the presence of copper. But in most cases the coloration is not stable; it rapidly fades, giving place to a turbidity which on standing or centrifugation is resolved into a blackish precipitate tinged with brown or blue, as if the solution still contained iron. The cause of this anomaly appears to be the presence of zinc which is known to accompany copper in the organs of plants. If ferrocyanide is added to a very dilute cupric solution acidified with hydrochloric acid and containing varying proportions of zinc sulphate, the phenomenon can be reproduced, and when the amount of zinc is double that of the copper a blue mass can be separated by centrifugation. The blue coloration attains its maximum of intensity and purity when the zinc is four or five times as abundant as the copper, becoming paler as the proportion is increased. This is one of the most sensitive reactions of copper, and it is only necessary for the solution to be free from nitric acid and iron. To apply the method in practice the ash is heated with sulphuric acid in a quartz capsule, the particles of silica and calcium sulphate are separated by centrifugation and the liquid is electrolysed. After twelve hours the cathode is washed with warm nitric acid and water, the liquid is evaporated, the residue calcined and taken up with hydrochloric acid. Then sulphate of zinc (0·25 mg., *i.e.*, 2 drops of a solution containing 1·104 grms. per cent) and a drop of 10 per cent potassium ferrocyanide are added. If copper is abundant, in which case it would have been visible on the cathode at the end of the electrolysis, a pink coloration, which soon turns blue, appears. If the amount of copper is less than 0·01 mg. the blue coloration appears after some minutes and the depth of the coloration of the precipitate obtained by centrifugation gives an indication of the amount of copper present.—*Comptes Rendus*, 1919, clxviii., 489.

Method of Treating Beryl for the Extraction of Glucina.—H. Copaux.—Beryl usually possesses a composition very close to that corresponding to the formula $Al_2O_3.6SiO_3.3BeO$, *i.e.*, 67 per cent of silica, 19 per cent of alumina, and 14 per cent of glucina. It is very refractory towards acids, but is acted upon by caustic alkalis, which at a temperature of about 400° transform it into a silico-aluminate of glucina and alkali, which is then readily attacked by acids. This method of opening up the mineral has the disadvantage of necessitating the elimination of the 67 per cent of silica which is present in the gelatinous form. The author has discovered a method of treatment of beryl which depends upon the action of sodium fluosilicate at a temperature of about 850°. Sodium fluosilicate Na_2SiF_6 is a white crystalline powder which is decomposed by heat at about 750° giving sodium fluoride and silicon fluoride, a very active gas which attacks the glucina giving glucinum fluoride $2BeO + SiF_4 = SiO_2 + 2BeF_2$. The latter then forms sodium fluoglucinate with the sodium fluoride $2BeF_2 + 4NaF = 2BeF_4Na_2$, which is soluble in water. The alumina by an analogous reaction is transformed into sodium fluo-aluminate, which is hardly soluble in water. Thus when the product of the reaction is taken up with boiling water all the glucina goes into solution. To purify the product the aqueous solution is treated with a small excess of boiling caustic soda, which precipitates simultaneously glucina, alumina, and silica, carrying down fluorine. The precipitate is redissolved in sulphuric acid, concentrated to expel the fluorine, and then the glucina is crystallised as sulphate $BeSO_4 + 4H_2O$, which is not isomorphic with either aluminium or ferric sulphate, which may be present in small quantities. By this method about nine-tenths of the glucina in the mineral is recovered. To determine the glucina in beryl 5 grms. of the finely powdered mineral are mixed with 20 grms. of sodium fluosilicate and heated for thirty to forty minutes to 850° in a graphite crucible. After cooling the powdered mass is taken up three times with boiling water and the aqueous liquid after filtration is made up to 1 litre; 300 cc. are then evaporated in a platinum crucible with excess of sulphuric acid till white fumes are evolved. The mass is then taken up with water and precipitated with ammonia. If iron is present in considerable amount the precipitate is dissolved in acetic acid, and the iron is removed by β-nitroso-naphthol. The filtered liquid is then reprecipitated with boiling ammonia, and the new precipitate, which consists of glucina, a little alumina and silica, is washed, dried, and weighed and then treated with a few drops of hydrofluoric and silicic acids to drive off the silica. After evaporation the alumina is removed by fusing the residue with three times its weight of sodium carbonate, extracting the sodium aluminate with water, and finally weighing the insoluble residue of glucina.—*Comptes Rendus*, 1919, clxviii., 610.

Reagent for and Method of Determining Ozone.—Louis Benoist.—As the phenomenon of fluorescence can be detected optically with great accuracy the author suggests a method of determining ozone based upon its action on fluorescine. If some cubic centimetres of a very dilute solution of fluorescine are introduced into a flask of slightly ozonised oxygen, after a few seconds the fluorescence absolutely disappears and the reagent is decolorised. If the solution is more concentrated the fluorescence disappears, but the colour of the reagent is only reduced to pale yellow. Pure oxygen has no effect. The traces of nitrous fumes contained in the air have no effect upon this new reagent, but chlorine does decompose fluorescine. On the other hand, its presence is very easily detected by other means and the gas can then be eliminated. The same applies to carbon dioxide, which destroys fluorescence when concentrated. The reaction appears to take place between two molecules of ozone and one molecule of fluorescine, the ratio of the weights being $\frac{96}{332} = 0{\cdot}29$. The least weight of ozone detectable by this method would thus be one-third of the least weight of fluorescine which would give an appreciable fluorescence. A Nernst or other lamp giving a very white light is enclosed in a dark box having two contiguous openings in the lid, in which are two colourless glass tubes; one contains the solution of fluorescine and the other control tube contains distilled water only. The caustic by refraction is observed in each tube, the one containing fluorescine exhibiting a distinct fluorescence. This method of determining ozone is very sensitive and possesses the advantage of requiring only one solution. The product of the reaction appears to be easily destroyed by heat, but the original fluorescine is not reformed; the addition of ammonia does not cause the reappearance of the fluorescence, and the final weight of the product after drying is only a very little less than that of the original substance. The product without being explosive appears to be in some way related to the ozonides.—*Comptes Rendus*, 1919, clxviii., 612.

NOTES AND QUERIES.

, Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Particulars and references are desired of the Ogston method for the analysis of citrate of lime.—(Reply to A. C.).

MEETINGS FOR THE WEEK.

Monday, 5th.—Royal Institution, 5. (General Meeting).
Tuesday, 6th.—Royal Institution, 3. "British Ethnology—The People of Wales and Ireland," by Prof. A. Keith.
Wednesday, 7th.—Royal Society of Arts, 4.30. "The Supply of Electricity," by J. Somerville Highfield.
Thursday, 8th.—Royal Institution, 3. "Clutches," by Dr. H. S. Hele-Shaw.
Friday, 9th.—Royal Institution, 5.30 "Chinese Turkistan—Past and Present," by Sir George Macartney, K.C.I.E.
Saturday, 10th.—Royal Institution, 3. "Chapters in the Psychology of Industry," by Prof. H. S. Foxwell.

THE CHEMICAL NEWS

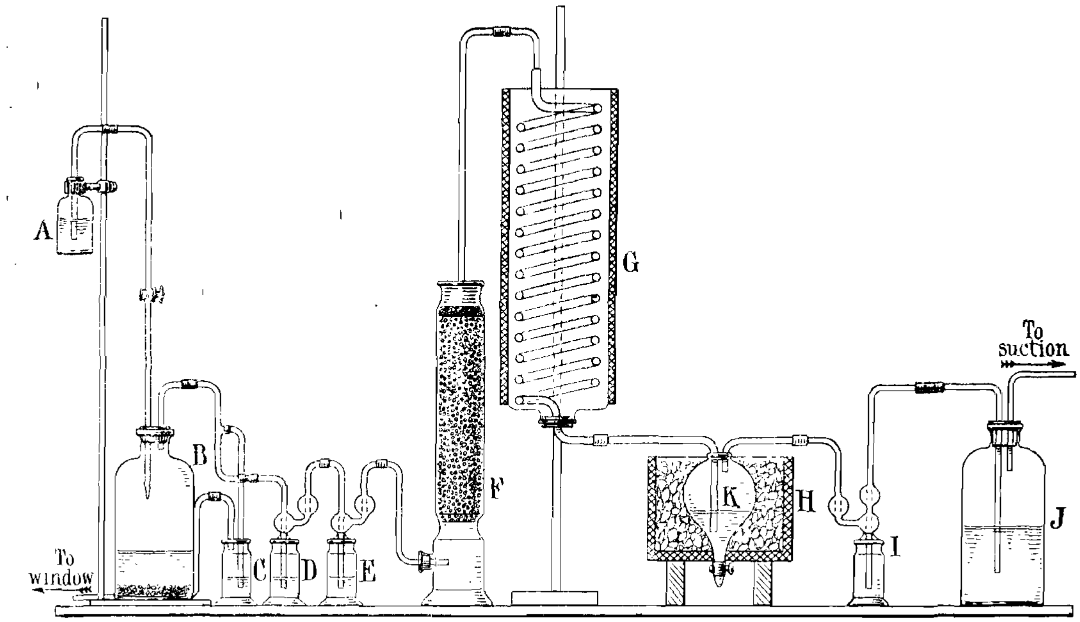
Vol. CXVIII., No. 3082.

A CONTRIBUTION TO THE CHEMISTRY OF TELLURIUM SULPHIDE.*

By AARON M. HAGEMAN.

(Concluded from p. 214).

The apparatus is shown in Fig. 1. The five-litre bottles B contained a supersaturated solution of sodium sulphide. Hydrogen sulphide was generated in this bottle by slowly dropping in 1 : 1 hydrochloric acid contained in the bottle A by means of a syphon and stopcock. It was purified from hydrochloric acid gas by passing through the sodium sulphide wash bottles D and E. After passing through the drying tower F, which contained calcium chloride, the gas was reduced to 0° C. by passing through the coil condenser G, which was completely surrounded by a cooling mixture. After cooling to 0° C. it entered the reaction chamber K, which consisted of a 500 cc. separatory funnel



contained in an asbestos-covered iron box with the stem and stopcock protruding through the bottom of the box. The box was completely filled with a cooling mixture for one hour before and during use, thus insuring that all parts of the reaction chamber with which the precipitate might come in contact would be at 0° C. Precipitations were carried out in the presence of 100 cc. of carbon disulphide, into which the precipitate was forced as formed by a constant whirling motion of the box during the introduction of hydrogen sulphide gas. After allowing the precipitate to stand in contact with the carbon disulphide the desired length of time, the carbon disulphide and the precipitate which had collected in it were drawn off through the stopcock on a large Gooch filter. The Gooch crucible also was jacketed and surrounded by a freezing mixture.

The advantages of this apparatus deserve mention. The gas was thoroughly cooled to 0° C. before entering the reaction chamber by passing through the long coil condenser surrounded by ice and water. The rate of flow was not great, owing to a fine jet between B and D, but was uniform. The reaction chamber was at 0° C. by being completely surrounded by the cooling mixture. After extraction, the carbon disulphide and that part of the precipitate that had actually been extracted could be drawn away. There was always a small amount of precipitate which remained in a fine suspension in the water above the carbon disulphide which was not extracted, but this never reached the filter. Moreover, the difficulty of filtering two immiscible liquids was overcome. The filter being jacketed with the freezing mixture insured its temperature to be at 0° C., so that at no stage during the operation was the precipitate subjected to any temperature other than 0° C.

Using this apparatus, a final series of experiments was carried out which served as a check on the results previously given. The details of procedure may be described as follows:—A sample of tellurous acid, acidified with hydrochloric acid representing approximately 0·2500 grm. of tellurium, was placed in this apparatus along with 100 cc. of carbon disulphide. Hydrogen sulphide was passed in for three minutes. During this time the reaction chamber was shaken to transfer the precipitate down into the carbon disulphide as formed. At the end of nine minutes the carbon disulphide and precipitate contained in it were passed rapidly through a suction filter consisting of a Gooch crucible fitted with a small disc of filter paper. One minute was thus allowed for the filtration. The suction of the precipitate was continued for ten minutes to remove the last traces of carbon disulphide. The precipitate thus collected was removed from the paper, placed in a P_2O_5 desiccator, and evacuated overnight. A sample of the precipitate was then weighed carefully, oxidised with fuming nitric acid in the cold, and the nitric acid removed by careful evaporation at 80° C. The residue was taken up in 10 per cent hydrochloric acid and the exact tellurium content determined. A short table of results follows:—

* Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xli., No. 3.

Wt. of Te found. Grm.	Required for TeS_2. Grm.	Required TeS. Grm.	Wt. of TeS ppt. Grm.	S in Te-S ppt. Per cent.
0·1824	0·2740	0·2282	0·2682	31·98
0·1650	0·2478	0·2063	0·2424	31·90
0·1168	0·1755	0·1461	0·1708	31·62

These results appear to be in fair agreement with those yielded by the previous method. Hence, since the weights of tellurium and sulphur found far exceed the weights required for TeS, the only conclusion at which one can arrive is that TeS is not formed primarily by the action of hydrogen sulphide on tetravalent tellurium. This is in direct contrast to the results obtained by Snelling (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 802).

A Study of the Conditions Necessary for the Existence of TeS_2.—It will be noted that all data thus far presented have shown that TeS does not exist. Moreover, the weights of tellurium and sulphur obtained have approximated the weights necessary for the compound TeS_2. Furthermore, the colour of the precipitate first produced is invariably a red-brown. At 25° C. the duration of this colour is short, a grey-black colour rapidly developing, accompanied by the coagulation of the precipitate into granules. At 0° C. the precipitate retains its red-brown colour for a considerably longer period. In view of these facts and remembering that ten minutes after precipitation carbon disulphide removes a definite amounr of sulphur, its seems justifiable to assume that TeS_2 is first produced, but the affinity between sulphur and tellurium being very weak, dissociation takes place, and the chemical compound separates partially into its elements.

Since the affinity between elements of this character is usually increased at reduced temperatures, a preliminary experiment was carried out at about —40°. A bath of acetone was cooled to —40° C. by the addition of solid carbon dioxide. In it was placed a large test-tube containing 50 cc. of carbon disulphide and 20 cc. of tellurium chloride dissolved in concentrated hydrochloric acid. After the contents of the tube had assumed the temperature of the bath, hydrogen sulphide cooled to 0° was passed in. The red-brown precipitate produced was forced into the carbon disulphide as completely as possible. After standing at this temperature for one hour, the precipitate still remained a red-brown and the carbon disulphide still remained perfectly colourless, showing no indication of dissolved sulphur. A second tube containing 50 cc. of carbon disulphide was also cooled to —40° C. To it was added some previously prepared tellurium-sulphur precipitate which had been allowed to decompose at room temperature. This carbon disulphide immediately assumed a yellow colour, indicating the presence of dissolved sulphur.

Although this experiment was only qualitative it indicated that tellurium and sulphur form a stable compound at this temperature, since it was shown that small amounts of sulphur impart a distinct yellow colour to carbon disulphide. If this be true, it was of interest to determine the highest temperature at which this compound was still stable.

For this purpose determinations were carried out at —10°, —15°, and —20°, respectively. In each case the precipitate was gelatinous, thus differing from the precipitates obtained at 0°. In each experiment, too, the extraction with carbon disulphide lasted one hour instead of ten minutes, as previously. During this time the precipitate remained a red-brown colour, showed little tendency to coagulate, and was dissociated but slightly at —10° and —15°. At —20° complete stability apparently existed. The following tables show this to be the case.

Wt. of Te, Grm.	Required for TeS_2. Grm.	Required for TeS. Grm.	Wt. of Te-S ppt. Grm.
	—10°.		
0·1488	0·2236	0·1861	0·2114
0·1165	0·1750	0·1457	0·1691
0·1450	0·2178	0·1814	0·2074
	—15°.		
0·1594	0·2395	0·1995	0·2368
0·0882	0·1325	0·1104	0·1299
	—20°.		
0·1406	0·2106	0·1759	0·2103
0·1102	0·1652	0·1376	0·1636
0·1132	0·1701	0·1416	0·1709

It would appear, therefore, that —20° is approximately the highest temperature at which the two elements, tellurium and sulphur, form a stable union.

The Action of Hydrogen Sulphide on Non-aqueous Solutions of certain Tellurium Compounds.—The preceding work has shown that a temperature of —20°, or below, is essential for the existence of a stable compound of tellurium and sulphur in aqueous solution. At higher temperatures the compound undergoes gradual dissociation into its elements. Although such a decomposition can scarcely be regarded as hydrolysis, the influence of the medium upon the formation and stability of this compound is of interest.

Three salts of tellurium were found to have a comparatively wide range of solubility in non-aqueous solvents, namely, tellurium tetrachloride, tellurium acid tartrate, and tellurium acid citrate. Of these three, the tetrachloride showed the greatest range of solubility.

The method of testing the solubility of these compounds in non-aqueous solvents consisted in adding to about 25 cc. of the solvent approximately 1 grm. of the finely divided tellurium compound. The mixture was thoroughly shaken and allowed to stand for at least one hour, after which any remaining solid was separated by filtration. The solvent was carefully evaporated from the filtrate, the residue taken up in dilute hydrochloric acid, and a test made for tellurium with hydrasine hydrochloride. In some cases hydrogen sulphide was passed in directly, the appearance of a red colour proving to be a good qualitative test for tellurium. Assuming that the solubility might in some cases be attributed to small amounts of moisture present in the solvent, when a liquid was found to dissolve tellurium tetrachloride, the liquid was subjected to careful dehydration by shaking with KOH, P_2O_5, or to desiccation by standing over these dehydrating agents until free from moisture. The nature of the liquid determines the method employed. A test of the solubility was then repeated in the absolutely anhydrous reagent, thus insuring that water played no part.

Tellurium tetrachloride proved to be soluble in benzene, toluene, methyl alcohol, absolute ethyl alcohol, normal butyl alcohol, amyl alcohol, benzylic alcohol, xylol, chloroform, and ethyl acetate. In petroleum ether, kerosene, benzaldehyde, acetone, isopropyl bromide, and carbon tetrachloride it was but sparingly soluble, while in carbon disulphide it was completely insoluble. Tellurium acid tartrate was found to be soluble in methyl alcohol, normal propiolic alcohol, ether, acetone, pyridine, and acetonyl acetone. It was sparingly soluble in acetonitride, aldehyde-cyanhydrin, acetone-cyanhydrin, acetoacetic ester, iso-butyric alcohol, ethyl alcohol, iso-propyl alcohol, fusel oil, acetic anhydride, and benzylic alcohol. The solubility of tellurium acid citrate may be expressed as follows:—Soluble in butyl alcohol, ether, absolute ethyl alcohol, ethyl alcohol, ethyl acetate, and amyl acetate, and slightly soluble in aniline, benzaldehyde, and acetone.

The combined solubilities of these three tellurium compounds offered a large number of mediums in which tellurium sulphide precipitations could be carried out. These solutions consequently furnished data which would either prove or disprove whether the medium in which the precipitation of tellurium sulphide is brought about is an influencing factor.

Hydrogen sulphide was passed into each solution of the tellurium compound in the organic liquid. At room tem

peratures the procedure consisted in precipitating the sulphide, washing it free from hydrogen sulphide with portions of the solvent, dissolving the precipitate in aqua regia, and making qualitative tests for tellurium and sulphur. In many cases, as with acetone, direct addition took place between the hydrogen sulphide and the solvent with the production of extremely obnoxious odours. No further work was carried on in such cases. In a large number of cases, especially where the tellurium compound in solution was the acid tartrate or acid citrate, colloidal solutions were obtained. This was overcome by passing in pure dry hydrogen chloride gas, which usually coagulated the precipitate. When the hydrogen chloride gas reacted with the solvent this procedure could not be used.

A red-brown precipitate at the moment of precipitation was always produced, which appeared identical with the one obtained in aqueous solutions. If allowed to stand at room temperature the precipitate rapidly changed to black, indicating dissociation. The precipitate always gave distinct qualitative tests for tellurium and sulphur.

Since the deportment of the tellurium sulphide precipitated in these solutions was so similar to its conduct in aqueous solution, hydrogen sulphide gas at 0° C. was passed into each of these solutions after they had been cooled to 0° C. As it was practically impossible to make quantitative determinations of the amount of sulphur that could be extracted at this temperature in a given time, and since carbon disulphide is miscible with practically all of these solvents, use was made of the rate of change of colour from red to black. It was difficult at first to determine just when this change in colour had taken place, as it is a gradual one, but practice soon showed that the rate of change of colour of the precipitate in these solutions very closely agreed with the rate of change in colour in aqueous solutions.

A final part of the work consisted in reducing these solutions to —20° C. and passing in hydrogen sulphide which had also been reduced to a low temperature. The red-brown precipitate then remained unchanged in appearance for one hour, which was considered a sufficient length of time to indicate that no dissociation was taking place and that the precipitate was stable at that temperature. In some cases the solutions froze before this temperature could be obtained, and in others so little of the tellurium compound remained in solution at that temperature that comparatively few solvents could be used. The solution of the tetrachloride in ether was very satisfactory.

All of the experiments made in non-aqueous solutions have shown that tetravalent tellurium is precipitated by hydrogen sulphide in these solutions exactly as in aqueous solutions. There is a tendency for the precipitate to separate in the colloidal form, but this may be prevented by the presence of dry hydrogen chloride. If the concentration of the tellurium solution is sufficient this condition is not encountered. The precipitate undergoes dissociation into tellurium and sulphur at the same rate at 0° C. as in aqueous solution, while if the temperature is reduced to —20° C. a stable compound TeS_2 exists between tellurium and sulphur.

Final Conclusions.

The results of this investigation have established the following facts regarding the production and stability of a sulphide of tellurium:—

1. The introduction of hydrogen sulphide into an aqueous tetravalent tellurium solution at room temperatures or below causes the immediate production of a red-brown precipitate represented by the formula TeS_2. The production of this compound is independent of the acid concentration.

2. At temperatures below —20° C. tellurium sulphide is a stable compound. At temperatures above —20° C., due to the weak affinity existing between these elements, dissociation takes place. At temperatures approximating —20° C. this dissociation is slow, while at higher temperatures dissociation takes place more rapidly. The degree of dissociation at any one time or temperature may be determined by the amount of sulphur that can be extracted with carbon disulphide.

3. Dissociation never continues to completion. The dissociated mass extracted with carbon disulphide always retains at least 0·95 per cent of sulphur. This sulphur does not exist as a sulphide of tellurium that is decomposed by hydrochloric or hydrobromic acid of any strength, nor does it exist as a variety of sulphur that is insoluble in carbon disulphide.

4. The compound TeS does not exist.

5. The production of the compound TeS_2 is independent of the medium in which it is carried out. The stability of this compound is solely a question of temperature.

PHYSICAL CHEMISTRY AND ITS BEARING ON THE CHEMICAL AND ALLIED INDUSTRIES.*

By Prof. JAMES C. PHILIP, O.B.E., M.A., Ph.D., D.Sc.

(Concluded from p. 208).

IT appears from the figures quoted that if the first portion of the change is left out of account practically constant values for the velocity coefficient are obtained, and it is a fair conclusion that the later portion of the change conforms to the law of mass action. The linear relationship between the time and the amount of change is observed only when the amount of enzyme is relatively small compared with the amount of carbohydrate. Certain recent work indicates that with purified malt diastase the abnormal period of the linear relationship is very short indeed.

The combination of hydrogen and oxygen at the surface of hot porcelain, and the action of diastase on starch, have been discussed in detail in order to illustrate some of the complications that arise in applying the mass action formulæ in cases of heterogeneous catalysis. Another very serious obstacle in this matter is the extreme difficulty, one might almost say the impossibility, of reproducing the catalyst in any desired condition of activity. In heterogeneous catalysis the scene of action lies in the surface layers of the solid catalyst, and it is well known in connection with technical catalysed reactions that the activity of the surface depends, in a very high degree, on the way in which the catalyst has been prepared and on the treatment it has received.

As an illustration of the influence which the previous history of the catalyst may exert on its activity, some observations made by Bone and Wheeler on porcelain surfaces may be quoted. These investigators found that previous treatment of such a surface with hydrogen stimulated quite notably its activity in connection with the combustion of hydrogen and oxygen. Preliminary treatment of the porcelain surface with oxygen appears, on the other hand, to reduce its catalytic activity. These statements are borne out by the figures in Table IX. k, the velocity coefficient, represents, as already explained, the rate at which the hydrogen and oxygen combine to form water. The porcelain surface was the same throughout, and the experiments were performed in the order shown.

TABLE IX.

Previous exposure to—	k
Hydrogen for 24 hours	0·0515
Oxygen for 24 hours	0·0305
Hydrogen for 40 hours	0·0592
Oxygen for 48 hours	0·0373
Hydrogen for 72 hours	0·0622

Normal value for k = 0·0430.

* Cantor Lecture (II.). Delivered before the Royal Society of A[rts], December 9, 1918. From the *Proceedings of the Royal Society of* [Arts], lxvii., No. 3451.

It is noteworthy that the stimulus imparted to the porcelain surface by preliminary hydrogen treatment survived a prolonged exhaustion of the apparatus, but gradually wore off as successive charges of electrolytic gas were circulated over the surface.

The significance of the previous history factor may be emphasised also in relation to one of the most important applications of catalysis on the technical scale, viz., the hydrogenation of oils. The development of this modern extensive technical developments, but work by others on the same lines showed that if hot oleic acid, in the *liquid* condition, is treated with a current of hydrogen in presence of a metal catalyst, such as finely-divided nickel, the hydrogen is absorbed and complete conversion into stearic acid is effected. Further, this method is applicable not only to the liquid unsaturated fatty acids, but also to their glycerides; *i.e.*, the liquid fats such as olive, linseed, and fish oils. As a result of this discovery the hardening

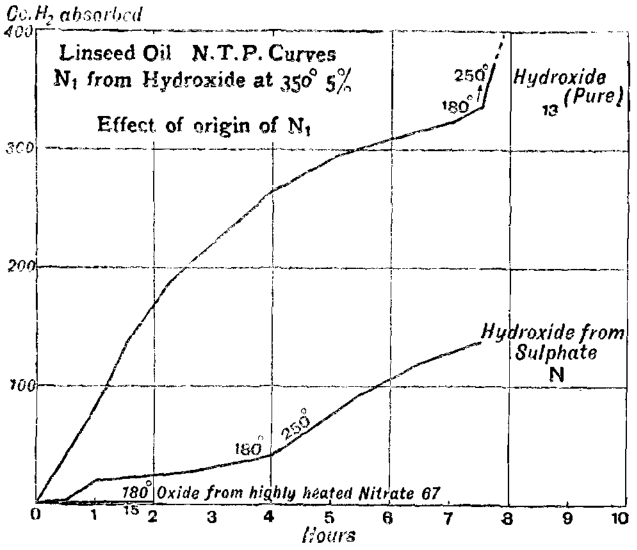


FIG. 1.

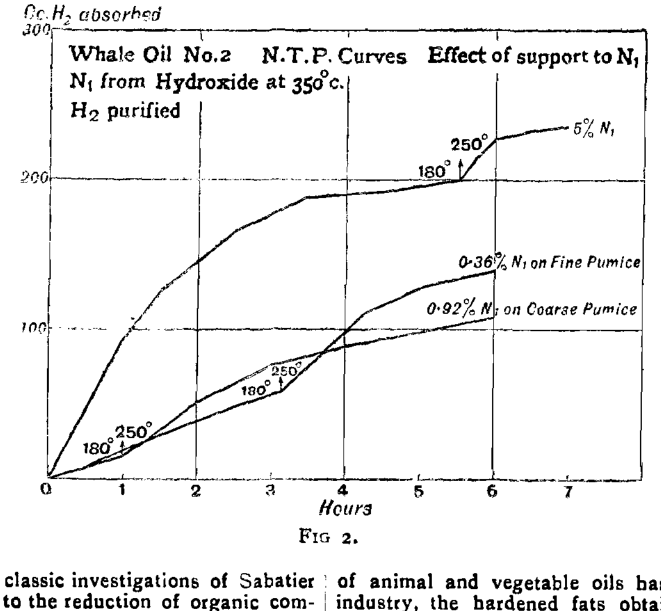


FIG 2.

industry is based on the classic investigations of Sabatier and Senderens relating to the reduction of organic compounds by hydrogen in presence of reduced nickel. Among other points which these workers established it was shown that the vapour of oleic acid, an unsaturated compound, when treated with hydrogen in presence of nickel at 280—300°, was almost completely converted into the corresponding saturated compound, stearic acid.

This observation, however interesting in itself from the purely scientific standpoint, would scarcely have led to of animal and vegetable oils has developed into a big industry, the hardened fats obtained by hydrogenation being employed in the manufacture of soap, or, in some cases, for edible purposes.

The very existence of this big industry is bound up with the successful preparation of catalyst metals, more especially nickel, and experience has shown that the activity of this metal is a function of its previous history. The nickel is in almost all cases obtained by reduction, but it turns out that the catalytic efficiency depends on

whether it is the oxide or the hydroxide which is reduced; it varies with the salt from which the oxide or hydroxide is obtained, and with the temperature at which the reduction is effected. The influence of some of these factors is made clear by the diagram shown (Fig. 1, Hehner), from which it appears that nickel prepared from the oxide, obtained in its turn by strongly heating the nitrate, is almost without catalytic activity in the hydrogenation of linseed oil. If the metal is prepared by reducing the hydroxide, obtained from nickel sulphate, there is a distinct improvement, but if hydroxide from nickel nitrate is reduced a catalyst of great activity results. Again, if nickel carbonate is ignited at 400—450°, and the resulting oxide is then reduced with hydrogen at 400°, a product of comparatively poor catalytic qualities is obtained; if, however, the ignition and reduction are carried out at 300° the resulting nickel is highly active.

All this may be regarded as very capricious behaviour on the part of the nickel, but certainly furnishes strong evidence as to the difficulty of reproducing a catalyst of a given degree of activity. That, as already stated, is one of the difficulties in the study of heterogeneous catalysis on quantitative lines.

The degree of sub-division of the nickel catalyst is naturally also an important factor. The hydrogenation presumably takes place at the nickel-oil surface, and the increase of surface which is involved in the progressive mechanical sub-division of a given weight of material may therefore be expected to lead to increased catalytic activity. One common method of securing greater surface extension of the nickel catalyst in the hydrogenation process is to use a porous carrier, such as kieselguhr or pumice. These materials may be impregnated with nickel salt, followed by precipitation of the hydroxide and reduction at a suitable temperature. The effect of such an increase of the contact surface is illustrated by the two lower curves in Fig. 2 (Hehner).

Other efforts to prepare a very finely-divided and therefore presumably highly active nickel catalyst have centred round nickel carbonyl. This compound, when mixed with the oil and heated to about 200°, decomposes completely and gives a fine suspension of the metal which is a very effective catalyst. There is, however, another manner in which nickel carbonyl may be used as the source of an active nickel. This process (Lessing) consists in *continuously* supplying nickel carbonyl along with the stream of hydrogen which is charged into the hydrogenation chamber. At the temperature which prevails there the carbonyl is decomposed, and the nickel at the moment of liberation presents a maximum surface development, and accordingly a very high catalytic power. It is said that excellent results are obtained even when the proportion of nickel to oil is as low as 1 : 1000.

Like other catalysts the nickel employed in the hydrogenation of oils is very sensitive to certain poisons, among which chlorine and sulphur are prominent. The most important question, however, which has emerged in this connection is whether carbon monoxide is to be reckoned as a "poison" for nickel, and whether, therefore, there is any objection to the use in the hydrogenation process of a hydrogen obtained from water-gas. Opinion appears to have differed on this point, but it now seems to be established that carbon monoxide exerts a marked poisoning effect on the hydrogenation of oils in presence of nickel. This conclusion may be based, for example, on Maxted's experiments in which separate charges of olive oil, each containing 1 per cent of a stock nickel catalyst, were agitated with pure hydrogen or a hydrogen contaminated with a known proportion of carbon monoxide. The volumes of hydrogen (in cubic cm.) absorbed by 10 grms. of oil at 180° in the various cases are recorded in Table X.

An examination of these results shows that the first traces of carbon monoxide have relatively the greatest retarding effect on the velocity of hydrogenation.

The features of heterogeneous catalysis may be further emphasised in connection with a technical process which is of great and growing importance at the present moment, viz., the oxidation of ammonia. This operation, although it has been known on the commercial scale since about 1902, assumed peculiar significance during the war, for obvious reasons, and it is stated that in Germany as much as 100,000 tons of nitric acid have been produced in this way annually by one process alone.

TABLE X.

Time in minutes.	Pure hydrogen.	Carbon monoxide (per cent).			
		0·25°.	0·5°.	1·0°.	2·0°.
5	86	72	67	58	28
10	143	122	111	93	57
15	194	159	142	116	76
20	248	193	168	136	91
30	348	252	213	164	114
50	515	352	281	215	146

The importance of securing other supplies of nitrates than Chili saltpetre has been recognised in this country, and steps have been taken to put the oxidation of ammonia on a sound technical basis. The United States Government, on its part, has allocated a sum of no less than £20,000,000 to the erection of factories for the production of nitric acid by the oxidation of ammonia.

The conversion of ammonia into nitric acid is effected, as a rule, with a platinum catalyst in the form of gauze or net, through which the mixture of ammonia and air is forced. Quite a good yield is obtained without continuously heating the gauze, but provision may be made for passing an electric current across the gauze, sufficient to maintain it at a dull red heat, say, 600 - 700°. The reaction is represented by the equation $4NH_3+5O_2=4NO+6H_2O$, and is accompanied by a considerable evolution of heat.

One of the most remarkable features about this catalytic combustion of ammonia is the very high yield obtained even when the passage of the gases is extremely rapid. Thus, with a mixture of 1 volume of ammonia and 7·5 volumes of air flowing over a 6 in. × 4 in. gauze at the rate of 20 cubic feet per minute, over 90 per cent conversion can be obtained. That such a brief period of contact of the reacting gases with the catalyst of the order of 0·01—0·001 second, should be sufficient for the occurrence of the change is indeed very striking.

It has been stated in connection with a description of the converters designed in this country during the war that an output of 1·5 tons of pure nitric acid per square foot of catalyst area per twenty-four hours, with an efficiency of 95 per cent, has been regularly achieved. Hence it has been calculated the output of nitric acid per grm. of platinum is no less than 15 kilogrms. in the twenty-four hours. This is a remarkable illustration of the first characteristic of a catalyst to which reference has already been made in this lecture, viz., that the amount of the catalyst may be extremely small compared with the quantities of the reacting substances transformed under its influence.

In relation to efficiency, the character and condition of the surface of the platinum catalyst is all-important. Platinum-black and sponge are both too active, and promote an oxidation of the ammonia in another direction, viz., to nitrogen and steam. Massive platinum, on the other hand, with a bright surface, is almost without catalytic activity, and something between this and black or sponge furnishes the most effective surface for the oxidation to nitric oxide.

New gauzes are not very effective catalytically, but are "activated" by passing an ammonia-air mixture at a bright red heat. The bright surface of the platinum becomes dulled in this process, and the catalytic activity increases.

It is, in view of what is generally known, not surprising that the platinum catalyst is very sensitive to certain foreign substances. The ammonia gas must be freed from

possible contaminations as phosphine, silicon hydride, hydrogen sulphide, and acetylene, each of which would "poison" the contact substance. It is found necessary also to filter the gases very thoroughly, since dust, especially if it carries with it particles of iron oxide, has a notably deleterious effect on the platinum. For this reason it is found advisable to avoid contact of the filtered gases with iron pipes, from which traces of oxide might be detached and carried along with the gas current; the converter and the piping which leads to it are therefore suitably constructed of aluminium. Provided that "poisons" are excluded by the precautions just indicated, the "life" of the catalyst is fairly prolonged; it is said that even when the oxidation process is carried on uninterruptedly that platinum gauze remains effective for several months.

The brief review which has been given of some prominent cases of industrial catalysis would lead up naturally to a discussion of the *modus operandi* of the catalyst, but this is somewhat outside the scope of the present lectures. Suffice it to say that, according to one view, the acceleration of a chemical change due to the catalyst is brought about by the rapidly alternating formation and decomposition of an intermediate compound or compounds of which the catalyst forms a part. Thus, for example, the effect of spongy platinum in promoting the combination of a mixture of hydrogen and oxygen is attributed to the primary formation of an oxide of platinum, which in its turn is reduced by the hydrogen, yielding water and the original metal. Similarly, the reduction of the unsaturated organic compounds by hydrogen in the presence of a nickel catalyst is supposed by some to be effected by the preliminary formation of nickel hydride.

Such a chemical view of the mechanism of catalysis can be defended only if the rate of formation and decomposition of the intermediate compound is greater than that of the uncatalysed reaction. In many cases, too, the participation of the catalyst in some intermediate reaction is, to say the least, highly improbable, and in such instances it seems that the catalyst performs some purely physical function. Reference has been made to the catalytic combination of hydrogen and oxygen at hot surfaces, and in this connection it is exceedingly difficult to believe that porcelain acts as a catalyst by undergoing alternate reduction and oxidation. Rather does the surface of the solid in such heterogeneous catalyses appear to provide for some condensation or concentration of the reacting gaseous or liquid substances, the actual chemical change taking place then with high rapidity. Although this view does not presuppose any chemical intervention of the catalyst it does not exclude the possibility that the *physical* condition of the surface may be altered by the reaction. Indeed, there is evidence in various cases that this actually occurs. When, for example, ammonia is passed over metals at high temperatures and so decomposed, the physical properties of the metals undergo notable alteration, even although no nitrogen has been permanently fixed. Again, the reader may be reminded of the oxidation of ammonia at a hot platinum gauze, in which connection it has already been pointed out that during "activation" the appearance of the platinum surface undergoes a distinct change, passing from a bright condition to a dull one.

Altogether, there is no single theory which can interpret every case of catalysis, and it is certain that in seeking an explanation for the mode of action of the catalyst, both physical and chemical factors must be taken into account.

Messrs. Krishnaswamier and Bros., of 863, East Market, Madura (S. India), Importers of Coal-tar Dyes and Chemicals, with a view to increasing business invite manufacturers to send them samples and prices of Coal-tar Dyes, Chemicals, and intermediate products.

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Continued from p. 212).

"Bunsen was the first to deny that water was colourless. Struck by the greenish-blue tint of the hot water of the Icelandic geysers, he poured pure water into a glass tube two metres long and blackened on the inside. He was able to detect a faint blue under these circumstances and concluded that water is actually blue. The other colours besides blue must then be due to foreign substances, or to the reflection of light from a coloured background. Bunsen did not go into details as to the way in which the colour changes would occur. Some twenty years later, Tyndall put forward the view that the blue colour of the sky is due to the scattering of light from numberless colourless particles suspended in the air. This suggested to Soret (*Ann. Chim. Phys.*, 1869, (4), xvii., 517) that the blue colour of the Lake of Geneva might be due to similar causes, and he found that the water sends out light polarised perpendicularly to the refracted rays of the sun. The analogy between the experiments of Tyndall and of Soret is so close that one may claim the existence in the water of transparent particles which may be the cause of the colour. Hagenbach repeated these experiments at the Lake of Lucerne, getting similar results (*Ann. Chim. Phys.*, 1870 [4], xx., 225). The following year, Tyndall himself examined water from the Mediterranean and from the Lake of Geneva, sent to him in London (*Naturforscher*, 1871, iv., 1). When a beam of light was passed through them, it became blue and the blue light was polarised. These waters are therefore not optically empty. These experiments seem to show conclusively that the water itself is colourless, contrary to the opinion of Bunsen; but this is not necessarily true. Soret himself points out that on cloudy days there was not a trace of polarisation and yet the lake was blue. This is sufficient to prove that reflection is not the sole cause of the colour of the water. Further, if the blue of the water were due to exactly the same cause as the blue of the sky, the light transmitted by the water should be a crimson red at least as intense as that which lights up the tops of the high mountains or the thin clouds through which pass the rays of the rising and setting sun. This is not the case, however, as Tyndall himself points out. Also Father Secchi has determined the absorption spectrum of sea-water and finds that the red and yellow are lacking (*Naturforscher*, 1868, i., 149). It is also well known to people who have been down in a diving-bell or who have visited the Swiss grottoes cut in the ice of the Rhone or the Grindelwald glacier that the light is bluish. There is so little red that faces appear livid.

"In 1848, H. St. Claire Deville analysed a large number of natural waters (*Ann. Chim. Phys.* [3], 1848, xxiii., 32), and he observed that the blue waters of the Swiss and the Jura lakes, when evaporated, leave residues which are only slightly coloured, while the green waters of the Doubs and the Rhine contain a considerable amount of organic matter, so that the soluble salts were coloured distinctly yellow when the water was evaporated. From this it appears that the green waters and still more the yellow or brown ones may owe their colour to the presence of a small amount of yellow mud. If pure water is really blue, a small amount of yellow colouring would be sufficient to change the colour to green or even to yellow. This same idea crops up again in a much later paper on the colour of water by Wittstein (*Vierteljahresschrift für praktishe Pharmacie*, 1861, x., 342). This chemist analysed the waters of many of the brooks, rivers, and lakes of Bavaria, and thought that he had proved that the brown or yellow waters contain more organic matter and are less hard than the green waters. He explains the

* From the *Journal of the Franklin Institute* clxxxvii., No. 3.

different shades of natural waters by assuming, with Bunsen, that pure water has a blue colour, that the mineral substances dissolved in the water have no effect on the colour, and that the different colours are due chiefly to dissolved organic matter. These organic substances are brown in colour and are essentially humic acids. They are kept in solution by the presence in the water of a sufficient amount of alkali salts. On this hypothesis a water containing very little organic matter would be practically blue, while the blue colour would change continuously to green, yellow, brown, and black as the amount of organic matter increased.

"It is worth while to examine this hypothesis. At first sight it seems an excellent one because it rests apparently on definite facts; but it is easy to show that the hypothesis does not follow necessarily from the analytical data. It is therefore without any firm foundation and does not solve the question. I shall not stop to discuss the question whether the organic matter is brown when it is in solution or whether it becomes brown and even black during the evaporation. In view of the description of the evaporation given by Wittstein, it seems probable that the deep colour is due to the action of heat. Such a discussion would be a waste of time. Let us rather consider the analytical data as shown in Tables II. and III.

("During the evaporation innumerable brown flocks form and become even darker. If heat changes the solubility of the organic matter, it may also affect the colour).

TABLE II.—*Brown waters* (*p.p.m.*).

	Organic Matter.	KOH and NaOH.	Ratio.
Ily	37·8	10·1	3·74
Regensee	21·4	15·4	1·39
Rachelsee	43·3	18·4	2·35
Ohe	111·4	12·8	9·0
Steckenbach ..	55·0	9·5	3·68
Höhenbrunnfilz ..	59·7	7·8	6·50

TABLE III.—*Bluish-green waters* (*p.p.m.*).

	Organic Matter.	KOH and NaOH.	Ratio.
Isaar	39·6	9·8	4·04
Brunnthaler Spring	65·6	4·7	13·97

"These figures show that the colour of the waters stands in no direct relation, either to the amount of organic matter or to the alkali concentration. The green Isaar contains more organic matter than four of the brown waters and also more alkali than two of them. The waters from the Brunnthaler spring show similar relations. It is also worth noticing that Wittstein gives no analysis of a really blue water, and consequently there is no real basis for a comparison. He also makes the general rule that greenish-blue waters are hard because of the small amounts of alkali which they contain while the yellow or brown waters are soft, and then he admits that the rule holds only for running water, because the waters of the Lake of Starnberg are extraordinarily soft although green. I add that the blue waters of the Rhone, where the river flows out of the Lake of Geneva, are also soft, as is shown by the large number of laundries along the river. It is evident that the colour is not different for running and for stationary waters. Wittstein's hypothesis therefore seems insufficient. It may be true, however, for some very deeply-coloured waters, because if these really hold a coloured material in solution or in suspension their colour ought to be dark.

Schleinitz attributes the change in the colour of sea-water to the greater or lesser amount of dissolved salts (*Naturforscher*, 1875, viii., 59). He noticed sudden changes in the colour of the sea when he was crossing from Ascension towards the Congo on board the *Gazelle*, in 1875. On August 23, 5° south latitude and 9° west longitude, the sea changed from blue to greenish. On the twenty-fifth it was bluish and on the twenty-sixth, in 5·5° south latitude and 5·5° west longitude, the sea became again deep green, changing to a dirty green and then to a brown as the ship approached the Congo. Later, on the voyage from the Congo to the Cape, the sea became green, then bluish-green, and finally bright blue. Each time that the sea became greenish Schleinitz found that its specific gravity decreased while there was an increase when the sea became blue again. From this he concluded that the bluest water contained the most salt and that the salt was the cause of the colour. Although this observation led to a false conclusion, it confirms some of the results which I have found, and I shall come back to it again.

"It is worth noting that in the waters of the Lake of Neufchatel, and also in the ice from the lake, J. Brun found an alga which is green, orange, red, or brown, depending on the different phases of its development, and turns black after death (*Jahresbericht über Chemie*, 1880, 1512). Its presence might well affect the colour of the water."

In order to determine the colour of pure water Spring took two tubes five metres long and about four centimetres inside diameter, coated with black on the outside. When distilled water from the laboratory supply was put into the tubes, the colour was a light green, very like that of a dilute ferrous sulphate solution. Some days later the tubes were filled with freshly-distilled water and the colour was a fairly pure sky-blue. After standing about seventy hours in the tubes this water was as green as the first, without having lost any of its clearness. This preliminary experiment shows that the distilled water of the laboratory is far from being pure, and contains substances which undergo changes, in that a blue water becomes green slowly. These foreign substances may be inorganic or organic; it is not impossible that they are living organisms. The following experiment is evidence in favour of this. "The two tube were filled with distilled water, but one ten-thousandth of mercuric chloride was added to one tube. At first both tubes were blue and there was no perceptible difference between them. After six days the water in one tube had become green, while the water containing the mercuric chloride had not changed in colour, and even after three weeks the blue colour was the same. Mercuric chloride was then added to the green tube and after three days a distinct change towards blue was noticeable. At the end of nine days no further change took place, and the water was distinctly bluish-green; but it never returned to a pure blue. Since mercuric chloride is one of the most toxic substances known, especially for minute organisms, there is certainly reason to believe that living organisms are to be found in the distilled water of the laboratory, and that the water also contains the food necessary for the development of these organisms. . . .

"Stas has shown that rain water or spring water, if distilled twice, gives a liquid which volatilises without leaving any residue if evaporated at once in a platinum vessel (*Bull. Acad. Roy. Belg.*, 1860, [2], x.). If this same distilled water is kept several days and then evaporated, it leaves a noticeable brownish-yellow residue, which burns completely at red heat in the air. Stas concluded that distilled water contains volatile organic matter which becomes non-volatile spontaneously in the course of a few days. This conclusion fits in well with my observations. So long as the distilled water contains the dissolved organic matter in a volatile state, the water is blue by transmitted light, but it becomes more and more green as the dissolved matter becomes changed by the action of organisms and ceases to be volatile. A similar fact has also been observed by P. Glan in his studies on the absorption of light (*Pogg. Ann.*, 1870, cxli., 66). He calls attention to the difficulties due to the presence of foreign matter which it is almost impossible to remove. He notes that after distilled water has stood several days in a closed vessel, it lets less light through and appears as though turbid.

"These preliminary experiments show that the distilled water of the laboratory is absolutely unfit for experiments like these, for it changes on standing. Stas has pointed out a method for obtaining pure distilled water (*Mém.*

l. Roy. Belg., 1865, xxxv., 110). It consists in distil- spring water with a mixture of manganate and per- ganate of potash, taking care to condense the vapour platinum cooler. Water prepared by this method ains no trace of non-volatile organic matter either n first distilled or later. I have made use of this method, ıg all sorts of precautions. Ordinary water was first :d with alkaline permanganate for four hours in a glass el. It was then distilled twice in an apparatus made :ely of platinum, and was collected in a closed silver . out of contact with the air. In order to clean the ıratus, three litres of water were distilled and thrown y. Then the first fifth of the final amount of water lled was used to wash the surface of the silver flask. ve satisfied myself that water thus prepared is volatile ıout residue. To show this I have polished the inside platinum crucible with precipitated and dried silica so) get a brilliant surface on which the least trace of lue would show. When the water was evaporated in closed crucible, no visible deposit could be detected he mirror surface, and I believe that one cannot say such water contains any non-volatile material.

When this pure water was poured into the tubes it is l to describe the purity of the blue colour which was ı. The only thing that could be compared to it is the t beautful blue of the sky on a clear day at the top of gh mountain when one is far above the mists rising ı the ground. When the tubes were allowed to stand .wo weeks, no change in the purity of the blue could .etected. The permanence of colour is perhaps a proof ıe extreme purity of the water. I have treated this ɛr by the Tyndall method, focussfng a magnesium ıe on one point of the tube by means of a concave 'or. Unless my imperfect apparatus has led me into r, the luminous cone was scarcely visible in the liquid. 'as difficult for me to say whether its path could be :cted or not. Whatever one may think on this point, :ems certain that the purest water which one can pre- : is a wonderful blue if one looks through a sufficiently k layer. Is this colour peculiar to the water or is it to a reflection of the incident light as is the case with blue of the sky? I think that everybody will reject any othesis as to the colour being fortuitous. Under the litions as arranged, one looked through the water ıg the axis of the tubes in the direction of the illumi- ng ray. If the blue were due to the reflection of light n otherwise invisible particles, the maximum intensity he blue colour should be found in a direction perpen- ılar to the luminous ray, which is just the opposite to ıt occurs actually. Further, on this assumption the ısmitted light ought to be red or mixed with red, which ot the case, the purity of the blue proving the absence red. In addition I have made another experiment ch seems to me conclusive. If the blue colour of water ot characteristic of this substance and if it is due to the sence of foreign matter coming from the air, it follows t any liquid would be blue like the water if treated in same way. In other words, there could be no colour- , liquid. I have distilled five litres of amyl alcohol for eral weeks in a glass vessel and exposed to the air of laboratory. In spite of this careless treatment, and in :e of the fact that the liquid had taken up a good deal lust, there was no sign of colour in the tube when the ɛr was five metres in thickness. Lack of material vented an examination of a layer ten metres in thick- s.

At first I tried crystallised acetic acid and absolute yl alcohol, but these substances were yellow when .mined in a five-metre layer. This yellow colour dis- ıeared gradually as the layer was made thinner without ıwing either green or blue. I am not certain, however, t these substances are really yellow, because acetic acid l ethyl alcohol are apt to contain empyreumatic sub- nces which are very difficult to remove. It seems tain from these experiments that the purest water one ı prepare is not colourless but has a blue colour due to an absorption in the yellow and not to a reflection of the incident light.

"We can now discuss the causes of the different colours of natural waters. Since analysis has not shown in any definite way the presence of green, yellow, or brown matter in the green waters, and since Wittstein himself admitted the absence of any yellow mud in the green water of the Lake of Starnberg, a different line of attack must be chosen. Five litres of pure, blue water were treated with a few grms. of a lime containing no iron and obtained by calcining Carrara marble. This lime water was quite clear after standing for five days. A solution of carbon dioxide in water was added until a precipitate was just barely visible. When placed in the tubes the water was then absolutely opaque. It would not have been any different if ink had been poured into the tube instead of this calcareous water. The water was taken out of the tube, diluted with pure water, and treated with carbon dioxide to precipitate the calcium carbonate and then to redissolve it as bicarbonate. Every now and then the current of carbonic acid gas was cut off and the water was examined in the tubes. The original opacity dis- appeared slowly, and the light which came through was first brown, then pale brown, yellow, green, and finally the liquid became blue again though with a touch of green after the carbonic acid had been run in for eighteen hours. With the combined action of carbon dioxide and calcium carbonate it is thus possible to reproduce all the colours of natural waters from complete opacity to a greenish-blue.

"As a further confirmation I have prepared a saturated solution of calcium carbonate and carbon dioxide in pure water, which was green when viewed through a five- metre layer. I then placed this in a vacuum tube to draw off some of the carbon dioxide and to cause a dissociation of the bicarbonate, after which the liquid was examined in the tube. Each time this was done the colour became more yellow. The green disappeared soon and finally the tube became opaque. A drop of hydrochloric acid brought back the greenish-blue colour. Similar results were obtained with barium hydroxide and carbon dioxide. With excess of the latter the water became brown, yellow, green, and bluish-green. Using hydrochloric or nitric acid instead of carbon dioxide the colour changes are obtained more rapidly. A solution of sodium silicate containing a little free silicic acid was opaque in a five-metre layer and brownish-yellow when a metre in thickness. When a concentrated solution of caustic soda was added to dis- solve the free silicic acid, the yellow colour disappeared. Pure water holding in suspension a little amorphous silver chloride is opaque or yellow, depending on the thickness of the layer. Ammonia dissolves the precipitate and removes the opacity or the yellow colour.

"These experiments warrant the drawing of several conclusions. A luminous beam of given intensity will not pass through a sufficiently thick layer of a liquid holding enough particles in suspension even though these are transparent or colourless. A tube containing suspended calcium carbonate, barium carbonate, silica, or silver chloride may be opaque to diffused daylight and yet let through light from the sun or from burning magnesium. The physical state of the suspended particles does not affect the phenomenon. If one pours water into ethyl alcohol containing a little dissolved amyl alcohol, a persistent tur- bidity is caused, due to the minute drops of amyl alcohol which do not dissolve in the water. By varying the amounts of ethyl alcohol and water for a given amount of amyl alcohol, one can change the degree of turbidity and make it as small as one pleases. It is evident that each drop of amyl alcohol is liquid and transparent, and yet such a turbid liquid is opaque for a definite thickness of layer and intensity of light; it is yellow if the light is more intense and colourless under a very powerful light. Similar changes take place if the intensity of the light is kept constant and the thickness of the layer decreases. The reason for this is easy to see. When a ray of white light passes through a medium which holds in suspension

an infinity of reflectors, each simple wave forming the white light is reflected independently of the others. If there is not total reflection the intensity of each wave will decrease with increasing thickness of the layer. Since the different colours constituting white light have not the same luminous intensity, the weakest will disappear first and the colour at the ends of the spectrum, the red and the violet, will be eliminated early, while the yellow, which is the most intense to our eyes, will outlast the others though weakened itself. One could probably explain the phenomenon in another way and say that when white light passes through an absorbing medium the yellow is the last to disappear.

"I will add that it is not necessary to have a liquid holding reflecting particles in suspension. A similar phenomenon occurs in the air. Everybody has noticed that the shadow projected by smoke or by condensing vapour on a white background is not merely grey; it always has a yellow-brown colour to which one gives the name of yellow smoke or brown smoke. A liquid holding a colourless substance in suspension appears white solely because of the reflected light. Milky lime water, though very white, is as opaque as ink, and the white colour shows merely that the light which illuminates it does not pass through it.

(To be continued).

ORDERS OF THE MINISTRY OF MUNITIONS.

Seeds, Oils, and Fats.

With reference to the Seeds, Oils, and Fats Orders dated May 1, 1917, May 9, 1917, and June 19, 1917, the Minister of Munitions hereby orders as follows:—

1. The operation of the said Orders is hereby suspended as on and from April 30, 1919, until further notice.

2. Such suspension shall not affect the previous operation of the said Orders or the validity of any action taken thereunder, or the liability to any penalty or punishment in respect of any contravention or failure to comply with the said Orders prior to such suspension, or any proceeding or remedy in respect of such penalty or punishment.

3. This Order may be cited as the Seeds, Oils, and Fats (Suspension) Order, 1919.

NOTICES OF BOOKS.

Hindu Achievements in Exact Science. By Benoy Kumar Sarkar. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. Pp. xiii+82. Price 1.00 dol. net.

This book has been written with the object of providing chronological links between the scientific investigations of the Hindus and those of the Greeks, Chinese, and Saracens, and giving an outlined comparative account of the scientific work of ancient and medieval India. The author believes that the pure mathematics of the Hindus, for example, were in advance of those of the Greeks, and that even some of the European discoveries of the sixteenth, seventeenth, and eighteenth centuries were anticipated by them, while the Hindu inquiries into natural science were not less exact and fruitful than those of the Greeks and medieval Europeans. In support of these contentions he gives in separate chapters short summaries of the chief discoveries of the Hindus, pointing out every case in which they anticipated the workers of other nations. The subjects of the chapters include the various branches of mathematics, astronomy, physics, chemistry, medicine, surgery, anatomy and physiology, natural history, &c., and it is pointed out that India possesses an extensive scientific literature, which is not more contaminated by superstitition than European literature of the same epochs.

Petrol and Petroleum Spirits. By Wilfred E. Gutten-tag, Capt.R.A.F., A.R.S.M., D.I.C., Assoc.Inst.M.M., A.M.Inst.P.T. With a Preface by Prof. Sir John Cadman, K.C.M.G., D.Sc., M.Inst.C.E. London: Edward Arnold. 1918. Pp. xi+135. Price 10s. 6d.

Users of petrol, such as aeronautical and automobile engineers, have hitherto had some difficulty in getting definite information as to the actual nature and properties of the substance without having recourse to the standard treatises on petroleum, which, being written for the technologist, naturally treat the subject from a highly technical point of view and are more comprehensive and full of detail than is probably required. This book exactly meets the need for a comparatively simple and untechnical account of petrol, and even students of petroleum technology may find that it is useful to them as an introduction to the study of larger works. A short account is given of the properties, origin, and refining of petroleum, and the rectification and refining of petrol are treated in greater detail, while methods of performing routine tests and determining the most important properties of petrol are fully described. Special attention is paid to the discussion of the particular properties which are necessary for various purposes, and the notes and comments on this subject are very valuable. A useful chapter gives some account of the applications of petrol as illuminant, solvent, fuel, anæsthetic, &c., and a bibliograpby gives the titles of some of the most important English and American books on petroleum and liquid and gaseous fuels.

BOOKS RECEIVED.

Inorganic Chemistry. By James Walker, LL.D., F.R.S. Pp. viii+236. London: Bell and Sons, Ltd. 1919. Price 5s. net.

T.N.T. By G. Carlton Smith. London: Constable and Co. 1918. Pp. vii+133. Price 8s. 6d. net.

Greece before the Conference. By Polybius. With a Preface by T. P. O'Connor, M.P. London: Methuen and Co. 1919. Pp. xxvi+120. Price 5s. net.

Annual Reports of the Society of Chemical Industry. Vol. III. 1918. Pp. 408. Issued by the Society of Chemical Industry.

CORRESPONDENCE.

COAL CONSERVATION.

To the Editor of the Chemical News.

Sir,—May I call attention to the important statistics recently laid before the Royal Society of Arts by Sir Dugald Clerk in his paper on "The Distribution of Heat, Light, and Power by Electricity and Gas," and urge that they be taken into careful consideration by the Government before any steps are taken to foster the use of electrical energy *as a heating agent.*

It is admitted that the provision of an ample and cheap supply of electrical energy for light and power is of great importance to our industries; and in regard to the waste of heat in the coal used for the generation of electricity for those purposes, it does not compare unfavourably with the manufacture of light and power at gas works. The consumer's choice of electricity or gas can here depend solely on cost and suitability.

But the figures given by Sir Dugald Clerk (confirming, as they do, those of Prof. J. W. Cobb in the *Edinburgh Review* for January last) make it clear that a most deplorable and avoidable waste of coal is entailed in the use of electricity as a source of heat. By the use of gas this waste can be avoided, and at the same time the smoke nuisance in our towns and the drudgery in our homes reduced to a minimum.

Broadly it has been shown that to give equal heating or cooking service to the consumer the use of electrical energy as generated to-day entails the destruction of four tons of coal as against one ton at the gas works; and that even if the suggested "super" stations realised the most optimistic hopes of their advocates in regard to coal consumption the comparison would be as 3 to 1 in favour of gas.

Moreover, the use of coal for the raising of steam at electric generating stations means the absolute destruction of all the valuable chemicals recoverable at gas works as by-products, which have so largely contributed to our success in the War, and are vitally important to our industrial and scientific supremacy.

These facts and figures cannot be ignored. They show that the community must depend, in the future as in the past, on both the gas and the electrical industries of the country to play their respective parts in our industrial and domestic economy. Any idea of "doing everything by electricity" cannot be seriously entertained by practical men and women.

I could add much as to the practical drawbacks that would attend the proposed concentration of production in a few "super" stations, some of which were pointed out by the Chairman of the City of London Electric Lighting Company the other day; but my immediate object is to call attention to the gross waste of our national coal resources that would be entailed in the use of electricity *as a fuel.*—I am, &c.,

D. Milne Watson,
President of the National Gas Council.

39, Victoria Street, London, S.W. 1.
April 26, 1919.

EMPLOYMENT OF OFFICERS. CAMBRIDGE UNIVERSITY APPOINTMENTS BOARD.

To the Editor of the Chemical News.

Sir,—In the six or seven years before the War the Cambridge University Appointments Board had been successful in finding places for a considerable number of young Cambridge graduates in industrial and commercial organisations, as well as in professional work. Some of these men were trained in the science, engineering, or agricultural schools; others obtained their places as the result of general ability, apart from any technical training. The object of the Board is to recommend to employers young Cambridge men who are known to us as being possessed of character and ability, and to combine a high standard of selection and a relatively wide field of choice with something like or more than the weight of a private recommendation.

Now that the University is beginning to assume its normal aspect, may I be permitted to remind our friends that we are again able to make recommendations, and to express the hope that many employers as yet unknown to us may be added to the list.

We are faced at the present moment with the problem of placing in employment many young officers who had just completed their University career in 1914, or broke it off in order to fight. It is these, the volunteers of 1914 and 1915, who we are just now especially anxious to place. Some are of exceptional ability. Many, but for the War, would have found their way quite normally to industrial and commercial openings, and by now have made reasonable positions for themselves. They have now to start a year a year or two older, but often with greatly developed powers, and sometimes with experience which will be of direct use in their future careers. We are in touch also with a certain number of officers rather older than those mentioned above, who had already obtained some experience when the War broke out, but have now to start afresh.

We should be very glad to hear from employers who will trust us with making recommendations for industrial, commercial, or professional vacancies. Communications from employers are strictly confidential, and information is given to individual candidates only on the employer's instruction. Letters should be addressed to the Secretary, *University* Appointments Board, University Offices, Cambridge.—I am, &c.,

H. A. Roberts, Secretary,
Cambridge University Appointments Board.

Cambridge, May 1, 1919.

THE IMPERIAL WAR RELIEF FUUD.

To the Editor of the Chemical News,

Sir,—The claims arising out of the War which are least adequately met are those relating to the widows and orphans of our Sailors and Soldiers. The allowances to widowed mothers, who have to bring up families, hardly provide the necessaries of life in these times when food and clothing are so very costly.

The allowances given to the wives and childen of the men in the Navy and Army are not sufficient to meet their needs, and a widespread desire has been expressed that these should be supplemented. The Imperial War Relief Fund, which is carefully administered, grants such sums as will increase the allowance to an amount which will more adequately provide for the home.

The objects of the Fund are wide enough to meet the many cases of hardship which are excluded from the scope of other agencies. It seeks to give "Something Extra" to whose whose needs are not otherwise met, and who, apart from this Fund, would not receive the consideration they deserve.

Each contributor may recommend cases up to the amount of his subscription. Any donation which you may send for this necessary and patriotic object will be greatly appreciated.

Cheques should be made payable to the "Imperial War Relief Fund, and sent to the Hon. Treasurer, the Marquess of Breadalbane, K.G., the National Provincial and Union Bank of England, Ltd., 15, Bishopsgate, London, E.C. 3.—We are, &c.,

Beresford (Admiral), Hon. President.
Breadalbane, Hon. Treasurer.

NOTES.

The Ninth Annual May Lecture of the Institute of Metals will be delivered by Prof. Soddy, F.R.S., on "Radio-activity," at Caxton Hall, Caxton Street, Westminster, on Monday, May 19, at 8 p.m.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on May 5, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Col. G. Duff Baker, Mrs. Edward Bryce, Mr. C. E. Scott Dickson, Miss H. Newton Drew, Capt. A. Glyn Egerton, the Viscountess Glenconner, Mr. R. Owen Jones, Mr. K. S. Murray, Mrs. Pretyman-Newman, Mr. J. R. Pretyman-Newman, Mr. J. J. Stewart, Mrs. Street, and Mrs. Evelyn Whittard were elected Members. The Secretary announced the decease of Sir William Crookes, O.M., LL.D., F.R.S., and Sir Frank Crisp, Bart., Members of the Royal Institution, and Resolutions of Condolence with the Relatives were passed. The Secretary also announced that His Grace the President had nominated the following gentlemen as Vice-Presidents for the ensuing year:—Dr. H. E. Armstrong, Sir William Phipson Beale, Bart., Dr. J. H. Balfour Browne, K.C., Dr. W. C. Hood, the Hon. Sir Charles Parsons, Sir James Reid, Bart., Sir James Crichton-Browne (Treasurer), and Brig.-General E. H. Hills (Secretary).

Royal Institution.—The Annual Meeting of the Members of the Royal Institution was held on Thursday afternoon, May 1, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The Annual Report of the Committee of Visitors for the year 1918, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Report of the Davy-Faraday Research Laboratory Committee was read. Twenty-four new members were elected in 1918. Sixty-three Lectures and nineteen Evening Discourses were delivered in 1918. The books and pamphlets presented amounted to about 171 volumes, making with 404 volumes (including periodicals bound) purchased by the Managers, a total of 575 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—President—The Duke of Northumberland; Treasurer—Sir James Crichton-Browne; Secretary—Brig.-General E. H. Hills; Managers—Dr. H. E. Armstrong; Sir W. Phipson Beale; Horace T. Brown; J. H. Balfour Browne; Dr. J. A. Fleming; Major J. Dundas Grant; Col. John Gretton; the Right Hon. Viscount Hambleden; Dr. Donald W. C. Hood; H. R. Kempe; the Hon. Sir Charles Parsons; Sir James Reid; Dr. J. Emerson Reynolds; James Swinburne; Sir Thomas Wrightson. Visitors—Sir W. H. Bennett; W. R. Bousfield; John G. Bristow, Frank Clowes; Edward Dent; Sir James J. Dobbie; J. Hunter Gray; W. A. T. Hallowes; F. K. McClean; W. R. Malcolm; T. C. Owen; Richard Pearce; Sir Edward E. Pearson, Hugh Munro Rose; and Joseph Shaw.

Trade Catalogues for Palestine.—The Chief Administrator, Occupied Enemy Territory Administration for South Palestine, desires to obtain as many catalogues as possible upon numerous import lines, all of which should find a profitable market in Palestine. Facilities for inspecting these catalogues will be offered to interested parties in Jaffa, Haifa, and Jerusalem, and it is conceived that they will tend in no small measure to the replacement of enemy importation by United Kingdom goods. The main object is to draw enquiry; the question therefore of uncertain catalogue prices, he states, should not debar the sending of trade literature. Actual prices and delivery can be settled by correspondence with the manufacturers and gradual substitution of newer catalogues. Catalogues in the three principal languages of the country, English, French, and Arabic, are much appreciated, and were a great feature in the German pre-war trade propaganda. The following are the principal imports required, and it is suggested that suitable firms should send their catalogues addressed to Headquarters, Economic Section, O.E.T.A., Jerusalem:—Agricultural machinery and implements; Flour mill installations; All kinds of motors; Furniture; Bedsteads; Enamelware; Pottery; Glassware; Lamps; Stationery; Hardware; Ironware; Articles of construction; Book-printing and book-binding machinery and types; Boots and shoes; Drugs and chemicals; Brushes for painting and household; Travelling bags and necessaries; Locks; Musical instruments; Typewriters; All kinds of tools; Engines for petroleum and gas; Perfumery.

Public Policy and the Chemical Industries.—The chemical industries of Canada and the United States no less than those of Great Britain and France were born out of the stress of the Great War. Without the successful reconstruction of these industries in the allied countries the war would have been lost, for science and brains, more than muscle, determined the outcome. The rapid establishment of factories producing explosives, miscellaneous chemical works, as well as munition plants and metallurgical works with their necessary laboratories, stands as one of the great miracles of the war. To create these the owners of industrial plants abandoned their ordinary peace operations and surrendered their rights for the national cause. Some of them found it profitable, while to others the change meant financial loss. To all it meant the breaking-up of old connections and a disruption of business when the war ended. When the creation of the war chemical industries was determined by the Anglo-Saxon nations it was well understood that never again would these nations be placed at the mercy of their enemies in the production of those chemicals that were recognised as key industries. From these cardinal facts it becomes essential to Canada, the United States, and Great Britain that what was demanded as vital to winning the war is now also vital, if the chemical industries are to be safeguarded during the era following the war. Otherwise, our last state will be worse than the first. The preservation and sound development of the chemical and metallurgical industries becomes, therefore, not a question of tariff, but a question of national safety. A number of these established for war purposes at a cost of millions of dollars, now find themselves faced with a serious problem. As they were established by Government action and Government command, so they ought to be secured by Government intervention during the period of reconstruction. This is required by common justice as well as the plain logic of the case. In Great Britain, France, and the United States the situation has been taken in hand by the control and regulation of imports affecting these industries. In Canada there has been a laxness in this control, and a situation has developed which demands a wise foresight if industries established at heavy cost are to be safeguarded during the transition period. Some facts on this situation will be given in another issue.—*Canadian Chemical Journal*, iii., No. 4.

The Potash Situation.—Deposited here and there over a great layer of rock salt extending through north and middle Germany, lie the beds of potash and other salts which in recent years gave Germany a world-monopoly of the potash supply. The deposits at Stassfurt, extending over a hundred square miles, became famous, as they contain not only potassium chloride, carnallite, a double chloride of potassium and magnesium, and kainite, a compound of magnesium and potassium sulphate, but other valuable salts, the production of which fell into the control of the Potash Syndicate. The syndicate's operations were "bossed" by the government, which regulated the amount allowed for export and the prices at which it should be sold in foreign markets. In 1914, 531,300 tons were allowed to be exported, while 635,000 metric tons were retained for German consumption. In 1904 extensive deposits of potash salts were discovered in Alsace, which to-day are under French control. These deposits are reported to contain a billion and a half tons of raw material, equal to 300,000,000 tons of pure potash. This is in the form chiefly of muriate of potash, easier to purify than the salts at Stassfurt. Owing to the destruction of machinery by the Germans during the war it will take a year or more to put the Alsace potash mines in proper working order, but when that is done the annual output will be 800,000 tons, which will be about ten times the production that was permitted to the Alsatian mines by the Germans before the war. In other words, the world will get from Alsace alone nearly 300,000 tons more than was allowed before the war. Meantime, as the result of the cutting off of German supplies during the war, there has been a keen quest for other sources of potash. A considerable amount has been, and will continue to be, recovered from the flue dust in cement works. Some has been made from the seaweed, kelp, but while this and some other sources have been used during the period when potash rose from 40 to 45 dols. a ton up to 400 and 450 dols. a ton, they are not likely to be much in demand when the product drops below 100 dols. a ton. Important deposits of potash salts have been found near the borders of Abyssinia, in the Italian district of Eritrea, and these reached an output last

year of 20,000 tons. Deposits also have been found in Spain at Cordova, Luria, and other places, and the brine and salt lakes of Nebraska and California are now worked for their potash contents. A great future source of potash exists in the felspar rocks in which Canada is rich, but the chemical problem involved in producing it from this source is yet to be solved on a commercial scale. On account of the fall in prices the present is a critical time for potash producers in America. It is reported that 100,000 tons of potash produced in Nebraska are in storage warehouses awaiting sale. The total production from the Nebraska is about 220,000 tons a year, equivalent to 50,000 tons of pure potash; the production of the California works at Searles Lake being about 10,000 tons of "actual" potash. Kelp yielded last year a little over 10 per cent of the domestic production of potash in the United States. Foreign potash cannot be brought into Canada or the United States in time for this year's use on the land, so that if the existing stocks are freely drawn on it would be better for the farmers in securing greater production, and would give a chance for some branches of the new industry to survive. The American War Trade Board announces that no potash from Alsace will be available on this side before June next—and even then the imports are to be regulated by licence. By these means it is expected that a collapse in prices will be avoided.—*Canadian Chemical Journal*, iii., No. 4.

MEETINGS FOR THE WEEK

Monday, May 12.

Royal Geographical Society. "Crete—Its Scenery and Natural Features," by A. Trevor Battye.
Ceramic Society, 7.30.

Tuesday, May 13.

Royal Institution, 3. "British Ethnology—The People of Wales and Ireland," by Prof. A. Keith.
Royal Horticultural Society, 3. "Bottling and Drying," by Vincent Banks.
Royal Photographic Society, 7. "Development Papers and Desensitisers," by W. C. Mann.

Wednesday, May 14.

Royal Society of Arts, 4.30. "Railway Transport in the United Kingdom," by H. Kelway-Bamber.
Institution of Electrical Engineers, 6. "Wireless in the Royal Air Force," by Major J. Erskine Murray.

Thursday, May 15.

Royal Society, 4. (Election of Fellows). "Area of Surfaces," by Prof. W. H. Young. "Change of the Independent Variables in a Multiple Integral," by Prof. W. H. Young. "Chemistry of Coal—Part I. Action of Pyridine upon the Coal Substance," by Prof. W. A. Bone, F.R.S., and R. J. Sarjant. "A New Method of Weighing Colloidal Particles," by Prof. E. F. Burton. "Value of the Rydberg Constant for Spectral Series," by W. E. Curtis.
Royal Institution, 3. "Intensive Cultivation," by Prof. F. Keeble.
Royal Society of Arts, 4.30. "Soil Deficiencies in India, with special reference to Indigo," by Prof. H. E. Armstrong.
Institution of Electrical Engineers, 6. "The Telephone Service of Great Cities, with special reference to London," by E. A. Laidlaw and W. H. Grinsted.
Chemical Society, 8.

Friday, May 16.

Royal Society of Medicine (Otology Section), 5. (Annual Meeting).
Royal Institution, 5.30. "Subantarctic Whales and Whaling," by Dr. S. F. Harmer.

RESEARCH FELLOWSHIP.

SCOTTISH TANNERS' FEDERATION.—Applications are invited for Post as RESEARCH FELLOW to the *Scottish Leather Trade.* Salary £400 per annum with a financial interest, to be mutually agreed upon, in discoveries of commercial value.—Address, S. T. F., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

DERBYSHIRE COUNTY COUNCIL.
COUNTY ANALYST'S DEPARTMENT.

WANTED, ASSISTANT TO COUNTY ANALYST.

Experience in Analysis of Foods, Drugs, Water, Fertilisers, and Feeding-stuffs essential. Preference given to applicants possessing Institute of Chemistry qualification or a Science Degree. Salary £250 per annum. For forms of application, particulars of duties, &c., send stamped addressed foolscap envelope to the undersigned.
Applications (endorsed "Analytical") must be upon the form provided, and must reach me not later than FRIDAY, MAY 30th.
Canvassing in any form will be a disqualification.

N. J. HUGHES-HALLETT,
County Offices, Derby. Clerk of the Derbyshire County Council.
Dated this 1st May, 1919.

UNIVERSITY OF MANCHESTER
(FACULTY OF TECHNOLOGY)

MANCHESTER MUNICIPAL
COLLEGE OF TECHNOLOGY

APPOINTMENT OF LECTURER IN PHYSICAL CHEMISTRY

The City Council and the University of Manchester jointly invite applications for a Lectureship in Physical Chemistry in the University of Manchester and in the College of Technology.

Salary: £400 a year, together with a bonus at a rate to be fixed from time to time.

Conditions of appointment and form of application may be obtained from the Registrar, College of Technology, Manchester. The last day for the receipt of applications is 14th June, 1919.

Canvassing, either directly or indirectly, will disqualify a candidate for appointment.

J. C. MAXWELL GARNETT,
Dean of the Faculty,
Principal of the College.

If in good condition, Sixpence per copy will be paid for any of the undermentioned numbers of the CHEMICAL NEWS which may be forwarded to this office:—

3048, May 24th, 1918.
3064, January 3rd, 1919.
3066, January 17th, 1919.
3068, January 31st, 1919.
3069, February 7th, 1919.
3070, February 14th, 1919.
3075, March 21st, 1919.

16, NEWCASTLE STREET, FARRINGDON STREET, LONDON, E.C. 4.

G. R.

BY DIRECTION OF THE DISPOSAL BOARD, MINISTRY OF MUNITIONS.

SURPLUS CHEMICALS FOR SALE.

The Surplus Government Property Disposal Board announces that it has for Disposal CHEMICALS of various kinds, such as are used, for example, in the Dyemaking, Textile, Explosives Firework, Paper-making, Paint, and many other industries. Consumers and other interested parties are invited to apply for Lists of the Chemicals to the CONTROLLER, Chemical and Explosives Section, Disposal Board, Storey's Gate, Westminster, S.W. 1.

THE CHEMICAL NEWS

Vol. CXVIII., No. 3083.

ON ACQUIRED RADIO-ACTIVITY.*

By Sir WILLIAM CROOKES, O.M., LL.D., D.Sc., &c.

Experiments with Cathode Rays.

1. About forty years ago I sealed in a vacuum tube a yellow diamond cut as a brilliant. This diamond was chosen because it phosphoresced in the dark after exposure to bright sunshine—*it also phosphoresced slightly under* the influence of ultra-violet light. In the vacuum tube, as the anti-cathode, it emitted a brilliant yellowish white light giving almost as much light as a candle. It was often exhibited to illustrate the glow of a diamond under the influence of cathode rays *in vacuo;* scarcely a week passed without the vacuum tube containing the diamond being exhibited to friends. It was by far the most attractive tube in my collection. After forty years of hard work the diamond has become much discoloured. It was of interest to see if the repeated bombardment, as the anti-cathode, in the vacuum tube had conferred radio-activity on the diamond. Accordingly I opened the tube, quickly removed the diamond, and in the dark put it on a sensitive film, a thin sheet of black paper intervening. Over the diamond was placed a pad of cotton-wool and a weight, to prevent the stone from shifting its position. After nine days' contact the film was developed. An exceedingly slight action could, with difficulty, be detected, showing that the off and on action for forty years had conferred practically no radio-activity on the diamond.

2. A sensitive electroscope was now made, with sulphur insulation. The fall of the leaf was observed with a small telescope having a photographed scale. The normal fall due to natural leakage was 5° in 165 seconds. A piece of a thoria gas mantle caused a fall of 5° in two seconds, and radio-active diamonds caused a fall in from two or three seconds to a fraction of a second. Tested in this instrument I found this special diamond to be entirely devoid of action.

Action of Cathode Rays on Diamond.

3. On one occasion when M. Moissan was in my laboratory I darkened some diamonds by means of cathode rays. One of these he took away, and subsequently reported the result of his experiments to the French Academy (*Comptes Rendus*, cxxiv., No. 13, p. 653, March, 1897). He heated the diamond to 60° C in an oxidising mixture of potassium chlorate and fuming nitric acid, prepared from monohydrated sulphuric acid and potassium chlorate fused and free from moisture (9, 12, 32). The action on the dark layer is very slow, requiring at least eight or ten days for its complete removal. There is at first produced graphitic oxide which at an increased temperature yields pyrographitic acid easily destroyed by nitric acid. Hence the variety of carbon which coated the diamond is graphite. The transformation of diamond into graphite requires the temperature of the electric arc, and the higher the temperature at which it is formed the greater is its resistance to oxidation. M. Moissan came to the conclusion that the temperature reached by the surface of the diamond blackened in my radiant matter ube was probably about 3600° C.

4. Six diamonds—having different degrees of phosphoescence under cathode rays—were tested in a Becquerel phosphoroscope to see if the order of intensity of the residual phosphorescence due to illumination with an arc light was the same as the order under cathode rays. All had a slight residual phosphorescence, but the order of intensity differed in the two cases.

* A Paper read before the Royal Society. From the *Philosophical Transactions of the Royal Society*, ccxiv., A, 521.

Action of Cathode Rays on various Mineral Substances.

5. For many years I have experimented on the changes produced in ordinary and quartz glass and various crystals by exposure to radium emanations and rays.

Considering the identity of the cathode discharge in a high vacuum tube with the β rays from radium, experiments were started to ascertain if the cathode rays would confer radio-activity in various solid bodies submitted to its influence. A vacuum tube was prepared with a removable window at one end to allow the contents to be exchanged for other bodies. In the tube were placed pieces of uranium glass, a crystal of ruby, a crystal of garnet, a piece of quartz, a plate of platinum and one of gold. The tube was exhausted to a high vacuum just short of the non-conducting point. On excitation the whole tube was filled with the green glow of phosphorescent glass, the ruby and uranium glass became very phosphorescent, the other bodies remained quite dark. After an hour's exposure to the cathode discharge the tube was opened, the objects quickly removed in the dark and placed on a sensitive film; the upper sides that had received most bombardment being placed downwards on the film. They were kept thus for eighteen hours and the film then developed. There was absolutely no impression of any of the bodies on the film. Thus it appears that the cathode stream will not confer radio-activity on the above-named bodies.

Action of Cathode Rays on Phosphorescent Bodies.

6. Experiments were next tried to see if earths and compounds which became strongly phosphorescent under the influence of the cathode discharge would thereby become radio-active. Some ignited yttrium sulphate, in the condition most sensitive to the cathode rays, and giving under their action a phosphorescent glow with a discontinuous spectrum, was pressed tightly into a shallow aluminium tray and exposed for an hour to the discharge in the vacuum tube. It was then removed and immediately covered with a sensitive film pressed down with a slight weight. After forty-eight hours in total darkness the film was developed. Only a very slight image of the yttria was visible. This result does not prove that the cathode stream had rendered the yttria radio-active, for there is always a residual glow in the yttria in these circumstances; it is not unlikely that the light of this glow, acting for the first hour or so of the forty-eight, might have been strong enough to impress the film (7).

7. Three shallow trays were filled—one with phosphorescent calcium sulphide, another with zinc sulphide, and a third with platinocyanide of barium. After subjecting them to the cathode stream in the above manner, they were removed and covered with a sensitive film, and kept in darkness for twenty-four hours. On development only an impression of the zinc sulphide was seen. As this sulphide also has a certain amount of residual glow after exposure to the cathode rays it is probable that the photographic action is only the result of this glow (6).

Action of Radium on Diamond.

In June, 1904 (*Roy. Soc. Proc.* lxxiv., 47), I read a paper before the Royal Society on the action of Radium on Diamond.

8. A few years later I repeated the original experiment, exposing two New South Wales diamonds to the action of the radium rays and emanations for a longer period. The diamonds selected were of an identical pale yellow, devoid of radio-activity. A quartz tube containing 15 mgrms. of pure radium bromide was well exhausted and sealed before the oxyhydrogen blowpipe. One of the diamonds was put close to the tube of radium and kept in its place with a piece of gummed paper. The other diamond was put away in a cabinet and kept far away from any radium compound. The two diamonds were thus left for a little more than six months. At the end of this time they were examined. No appreciable difference could be detected

in the colour of the two diamonds—the one that had been close to the tube of radium bromide not being darker than the one which had been away from radium the whole time.

Coloration of Diamond by α-Ray.

9. The diamond was now enclosed for seventy eight days in a tube containing radium bromide; at the end of the time it had acquired a bluish green colour. It was then heated for ten days in a mixture of fuming nitric acid and potassium chlorate so as to dissolve off any outer skin of graphite which might have contributed to the colour (3, 12, 32). The treatment brightened its appearance but did not alter the colour. The diamond was next put on a sensitive photographic film and kept there for twenty-four hours. On developing, a strong impression was seen.

β- and γ-Rays produce Phosphorescence.

10. This experiment shows that the alteration of the colour is not due to the phosphorescent state of excitement to which the diamond had been constantly subjected during eight weeks. The colouring action is cut off by a thin screen of quartz, whereas the phosphorescing action is kept up by rays which pass through quartz. It is therefore evident that the coloration is due to the α-rays, or atoms of helium, shot from the radium compound (26, 29, 33). The phosphorescence is produced by the β- or γ-rays (19, 26, 43), which readily pass through glass and quartz.

Persistence of Acquired Radio-activity.

11. The acquired radio activity of diamonds persists for a longer time than I have been enabled to measure, and resists the most violent treatment I have applied to them.

A large brilliant cut diamond of pure water assumed a fine green colour after having been kept for sixteen months (from May, 1904, to Sept., 1905) in a bottle and covered with powdered radium bromide. At the end of that time it was highly radio-active. This diamond has been carried about in my pocket, off and on, since 1905, and has been tested on a sensitive photographic film at intervals of a year or more. No appreciable difference in its radio-activity can be detected from that which it possessed when first removed from the radium bromide in Sept., 1905. Examined at the present time, nine years after its removal from the bottle of radium bromide, it is luminous in the dark, it rapidly discharges a sensitive electroscope when held near it, and produces scintillations on a zinc sulphide screen as if it were a radium compound.

12. A diamond of good water was selected from a stock of inactive stones, and put in a tube of radium bromide for seventy-eight days At the end of that time it had assumed a greenish colour, and was highly radio-active. It was then heated to 50° C. in a mixture of fuming nitric acid and powdered potassium chlorate for ten days, the acid mixture being daily renewed (3, 9, 32). The only effect of this acid treatment was to remove a slight dull darkening on the surface, and to render the green tint more brilliant.

After well washing and drying it was put on a sensitive film for five hours. On developing it was seen that the stone had made a good impression on the film.

13. The stone was then sent to a diamond cutter to be cut into a brilliant. On receiving it back it was quite white and free from trace of colour. The stone was then placed on a sensitive film and kept in darkness for twenty-two hours. On developing no impression was apparent, although, before cutting, the active diamond had impressed a film in five hours (12, 16).

Effect of Heat on Induced Radio-activity.

14. A New South Wales diamond which had always been kept away from radium salts, was tested in the electroscope (2) and found to give a fall in two seconds, the natural leak being 180 seconds. The stone was then put in a silica crucible and heated in an electric tray furnace until visibly red. No change was observed. After 5 minutes—at, say, 700° C.—it was allowed to cool. The time of discharge in the electroscope was found to be six seconds.

15. The diamond was then packed in a silica crucible with graphite and heated with a Meker burner to 700° C. several times, cooling and testing the diamond each time when cold.

Heated to 700° C. for 10 mins., and cooled, time of fall = 6 secs.
Heated to 700° C. for 15 mins., and cooled, time of fall = 10 secs.
Heated to 700° C. for 20 mins., and cooled, time of fall = 10 secs.
Heated to 700° C. for 20 mins., and cooled, time of fall = 30 secs.

It was now left for the night, and measurements resumed next day.

Heated to 700° C. for 60 mins., time of fall = 9 secs.
Heated in new graphite for 30 mins., time of fall = 7 secs.

New graphite again used.

Tested again after 48 hours, time of fall = 4 secs.
Heated to 700° C. for 30 mins., and allowed to cool for 2 hours, time of fall = 2 secs.

The diamond after the last measurement (2 secs.) was laid on a sensitive film and kept in the dark for twenty-one days; on development it gave a good image.

This experiment shows a temporary loss of activity by the heat treatment followed in a short time by complete recovery.

16. A Kimberley diamond, rather flat, octahedral shaped, was kept in a bottle of dry radium bromide for some weeks until it was quite green. By means of a steel wheel fed with diamond dust part of once face was cut away, and the surface of an adjoining face was just removed, the adjoining corner thus being freshly exposed diamond crystal. It was put on a sensitive film in such a position that it could be subsequently examined and compared with the developed image, so that the active portions of the surfaces, natural and ground off, could be seen. It was allowed to act for five days, when the film was developed. The result indicated very decidedly that where the surface of the diamond had been removed it was no longer radio-active (13).

Experiments with a very Active Diamond Crystal.

17. A fine crystal of diamond from Kimberley which had been kept in a bottle of radium bromide for some months was tested on a sensitive film and in the electroscope. It was found to be highly active, and was set aside for further experiments. It was luminous in the dark, quickly discharged the electroscope, and caused an inactive diamond held near it to phosphoresce. It was put on the surface of a screen coated with small crystals of barium platinocyanide, and caused scintillations the same as on a blende screen, but feebler (11, 26, 27, 30, 33).

18. A blende screen was made by coating a glass slip with very sensitive zinc sulphide. This was laid on the diamond, the ZnS side next the diamond; the scintillations were easily seen through it in all their characteristic appearance, with concentration at the edges and corners. A piece of aluminium sheet, 0·06 mm. thick, was moved about between the screen and crystal of diamond, and there was no doubt whatever that the aluminium stopped all the scintillations. It was absolutely dark where the aluminium covered the crystal.

19. The diamond (17) was then held in contact with the card back of a platino-cyanide of barium screen. The luminous patch due to β- or γ-rays, or to both, was quite evident, moving about as the diamond was moved. The sheet of aluminium foil used in the former experiment (0·06 mm. thick) was put between the crystal and the back of the screen, and there was little, if any, diminution in

the luminosity. It is therefore quite certain that the radio-active diamond gives off other rays besides α rays, and that the rays can penetrate aluminium 0·06 mm. thick and the card back of the screen.

20. The diamond (17) was put into various fluorescent solutions (uranine in water, Silberrard's *p*-nitroso-dimethyl-anilinenaphthaline compound, and quinine sulphate). It did not occasion the slightest fluorescence, although its own faint luminosity could be seen in the liquid.

21. The active diamond (17) was cemented to a plate of glass, and six small pillars of lead cemented round it the same height as the stone. The whole was inverted on a sensitive film, and kept in the dark for 2·25 hours. Another experiment was then tried with the same apparatus, only altering the position of the crystal so that the lead pillars were opposite the angles of the crystal. The exposure in this case was 6·5 hours. The pictures on development showed a strong radiation extending some distance round the diamond (six or eight diameters) and the lead pillars showed strong shadows.

22. The same experiment was repeated three times with the interposition of one, two, and three thicknesses of aluminium foil 0·01 mm. thick, each was exposed the same time (two hours), and all were developed together. Each showed strong action near the diamond. One thickness allowed the shadow of the lead pillars to be easily seen. Two thicknesses showed the shadow with difficulty, and three thicknesses only showed the shape of the diamond itself.

23. The crystal (17) was removed from its circle of lead pillars (21). A small cell of brass tube 0·5 inch in diameter had six slots cut in it with a file. The diamond was mounted in such a position that the three corners of the triangular surface that touched the film should come opposite three of the slots. These experiments show that the diamond is giving off β-rays copiously.

γ-Rays from the Radio active Diamond.

24. The diamond (17) crystal was fixed with its sharpest point upwards in a small thick cell of brass. Exactly over the point was a small hole 0·5 mm. in diameter and 5 mm. long. On the top was a piece of sensitive film enclosed in black paper. The whole was kept in the dark for three hours, when a fair image of the hole was obtained on development. The apparatus, with another sheet of sensitive film in it, was fixed between the pointed poles of a powerful electro-magnet, and a current of 30 amperes was passed through for three hours. The current was then shut off, and the film shifted sideways for half an inch, and the action of the diamond without the magnetism was allowed to go on for another three hours. It was then developed, and both spots appeared about the same intensity.

25. The diamond crystal (17) in its brass box had a thin plate of clear mica put over the hole, and a sheet of lead over that. All was wrapped in sheet lead, and so kept for about six months. There was an extremely faint but hardly appreciable darkening of the mica at the position of the hole.

26. After the above experiment the diamond was kept in its brass box for two years, and then laid on a sensitive film and kept there for three hours. On developing a spot of action was seen, showing that the diamond was still radio-active. It was removed from its brass cell and examined in the dark on a blende screen. It gave plenty of scintillations easily visible without a lens. Experiments showed that it still gave out, along with α-rays, also β- and γ-rays (10, 19, 42, 43).

27. A small light-tight box was fitted as a camera. The arrangements were such that the image on the sensitive film was 1·5 times the size of the object. A photograph of the radio-active diamond (17) was taken by the light of its scintillations on the blende screen (17, 26, 30, 33), giving forty-eight hours' exposure. The three bunches of luminosity come from the corners of the crystal that are in contact with the screen. The photographic impression is certainly discontinuous, appearing granular—corresponding to the granular character of the screen. It appears that the different grains shine and continue to shine by their own residual phosphorescent light under the impact of the α-particles. In a further experiment the diamond was illuminated by the arc lamp, and a photograph was made of the diamond crystal *in situ* as well as of the screen. This gave a good image of the stone, and also of the granular surface of the screen.

28. It is certain that, in addition to α-rays, the diamond (17) gives off a considerable amount of other rays (10, 19, 26, 42, 43). This is shown by the early experiments, where photographic images with the diamond were obtained through one, two, three, and four sheets of aluminium foil—each 0·01 mm. thick.

29. The crystal of active diamond (17), with which most of these experiments have been made, was examined crystallographically by Dr. Tutton, who reported to me that the crystal is an apparent octahedron—but composed of two supplementary tetrahedra showing on three of the edges the usual grooves where the interpenetration of the tetrahedra is not complete.

30. Experiments show that exposure of a zinc-sulphide screen to the impact of electrons from the negative pole in a vacuum tube does not cause scintillations. It appears that only α-rays (positive atoms) produce this effect (11, 17, 26, 27, 33); it was therefore interesting to see if scintillations could be produced by bombarding a sulphide screen with a stream of positive atoms produced in a "Thompson" tube. An apparatus was fitted up having a zinc-sulphide screen to receive the positive discharge—but no effect of scintillation could be observed.

(To be continued).

IODOMETRIC EQUIVALENTS.

By A. J. G. SMOUT, A.I.C.

THE data given below has been found very useful for pasting up in table form in the laboratory where thiosulphate and iodine titrations form part of the routine:—

Value.			Value.		
Iodine	× 1·2465	=	$Na_2S_2O_3$	Log.	= 0·0956
$Na_2S_2O_3$	× 0·8022	=	Iodine	,,	= $\bar{1}$·9043
Iodine	× 0·2953	=	Arsenic	,,	= $\bar{1}$·4703
Iodine	× 0·4722	=	Antimony	,,	= $\bar{1}$·6741
Iodine	× 0·1263	=	Sulphur	,,	= 1·1014
$Na_2S_2O_3$	× 0·2241	=	Chlorine	,,	= $\bar{1}$·3504
$Na_2S_2O_3$	× 0·5051	=	Bromine	,,	= $\bar{1}$·7034
$Na_2S_2O_3$	× 0·2747	=	Manganese dioxide	,,	= $\bar{1}$·4389
$Na_2S_2O_3$	× 0·1292	=	Pot. chlorate	,,	= $\bar{1}$·1113
$Na_2S_2O_3$	× 0·1461	=	Pot. perchlorate	,,	= $\bar{1}$·1647
$Na_2S_2O_3$	× 0·1096	=	Chromium	,,	= $\bar{1}$·0398
$Na_2S_2O_3$	× 0·4367	=	Lead	,,	= $\bar{1}$·

TRADE WITH THE LEFT BANK OF THE RHINE.—The announcement on this subject issued by the Board of Trade on March 14 is hereby cancelled, and it is announced that it will no longer be necessary for re-exporters to obtain licences from the Export Licence Department before shipping to the territories on the left bank of the Rhine in the occupation of the Associated Governments goods other than those included in List A and B of prohibited exports.—*Board of Trade Journal.*

REVIVAL OF INDIGO.

In addressing the Textile Institute, at Bradford, on February 27, on this subject, Prof. H. E. Armstrong took exception to the application of the adjective *natural* to indigo as redundant, also to the use of the expression *synthetic indigo*—as indigo never has been and never can be made artificially. Indigo is a mixed material, produced in a particular way from a plant, containing, in the case of well-made samples, about 70 per cent of the specific compound *indigotin*. This compound, not indigo, is the substance which is being manufactured and sold in an almost pure form. The term indigo should be used only in speaking of the natural product.

Indigo contains substances other than indigotin which have an influence in the dye vat, even if not actually dye-stuffs. It has been the studied policy of the German manufacturers to disregard these associated materials as of no account; all but the old conservative school of dyers have fallen into the trap; these latter have always maintained that indigo has special qualities, which give it an advantage, in dyeing heavy shades, over manufactured indigotin pure and simple. Probably, in future, this difference will be one of determining influence in the industry.

In trials made with special care to contrast indigo with synthetic indigotin, in dyeing heavy shades on loose wool, the former has been found to have the advantage to a very marked extent. Hydrosulphite vats (1500 gallons) were set with equal quantities of indigo and of synthetic indigotin paste, each containing 20 per cent indigotin, and equal quantities of loose wool were dyed simultaneously in the two vats in lots of 50 lb. at a time. In the case of the first two or three dyeings deeper shades were obtained in the indigo vat. In consequence, the addition of paste before dyeing each lot of wool was gradually reduced, and it was eventually found that equal depths of shade were produced when the amount supplied each time was 8 lb. of synthetic paste and only 6½ lb. indigo. Indigo produces a rather redder and brighter shade even when these proportions are used. The difference is being made the subject of systematic inquiry.

After considering the history of the introduction of synthetic indigotin and the position of indigo prior to the war, especially the great reduction in output of the natural product, Prof. Armstrong gave an account of the efforts made to improve the industry in India, in particular of late in Bihar, under the direction of Mr. W. A. Davis. It has been shown conclusively that a paste containing a standard proportion of indigotin, comparable with that in the synthetic paste on the market, is easily prepared, and that the only disadvantage it has arises from the presence of a certain proportion of insoluble matter. An organisation for the preparation of such paste has been established, and probably this material will be put on the market in competition with synthetic paste. Other forms, more easily transported, are in contemplation, however.

The process of manufacturing indigo has been much improved under Mr. Davis's direction—in particular the yield has been raised considerably by the recovery from the "seet" water of the finely divided, suspended indigo, which formerly ran to waste. This has been effected by adding Dhak gum.

The extraction process is being studied in every particular, especially on the bacterial side.

The crop has been a declining one of late years, owing to the diminished yield per acre, the occurrence of wilt disease, and the attack of the plant by an insect pest; also by reason of the difficulty of raising seed. A careful and extended survey of the results has led Mr. Davis to the conclusion that, at all events, the main cause of the decline is the depletion of the soils in available phosphate. Of late, even the Natal-Java plant has ceased to give a superior yield—the early success of this variety is shown to have been due to the fact that it is a very deep-rooted plant and was able to appropriate from the sub-soil the phosphatic supplies beyond the reach of the Sumatrana plant.

The future of the industry appears to be mainly contingent on the extent to which planters are able to apply phosphatic manures. Apart from the dyestuff it yields, the indigo plant is now of importance as a green manure; and as a leguminous crop it also has its definite, natural place in the rotation. It is clear that big crops can be obtained if proper agricultural conditions be secured, and that there will be no difficulty in raising seed. There is also reason to believe that improved varieties of the plant, giving an enhanced yield of indigo, will soon be produced. In short, improvements are foreshadowed in many directions, so that indigo may well recover its position and enter into effective competition with the artificially made somewhat imperfect substitute.—*Journal of the Society of Chemical Industry*, xxxviii., No. 7.

THE MANUFA TURE OF NEUTRAL SULPHATE OF AMMONIA.

A New Process.

Much interest has been shown at the present time in the matter of raising the standard of quality of the sulphate of ammonia generally supplied in this country. A strong movement is in being to persuade or compel manufacturers to eliminate the free acid which is a normal constituent of the sulphate ordinarily supplied. Such free acid is detrimental both to the transport and use of the salt. It rots the bags in which the salt is packed, and seriously impedes the agriculturalist in his efforts to secure an even distribution of the material in the soil.

It is not surprising that sulphate of ammonia which has been produced in the usual manner should contain free acid. The crystals of sulphate are deposited in a bath, which consists of more or less dilute sulphuric acid in association with a solution of sulphate of ammonia. As these crystals are removed from the bath they are, of necessity, surrounded by, and enveloped in, mother-liquor containing free sulphuric acid. Part of such acid drains away when the salt is allowed to rest; bnt a portion is left adhering to the crystals, and constitutes the free acid which is being objected to. In amount it varies from 0·3 to 1 per cent by weight of the salt; an average amount being about 0·5 per cent, where no special means are in use for its removal.

There are two ways by which this objectionable constituent may be got rid of. It may be eliminated, or it may be neutralised. For example, the salt may be washed with water, as in the following arrangement, for which a British patent was granted a year or two ago. There was an endless chain of perforated buckets dipping into the contents of the saturator, and raising therefrom the crystals of sulphate, which were met by a shower of water applied on the countercurrent principle—that is, the sulphate encountered progressively clearer or fresher water as it moved towards the discharge end of the conveyor. Thus the salt received a very effective washi g, eliminating the free acid. But, unfortunately for the success of the process, the washing cannot be applied without at the same time some of the sulphate itself being dissolved. This is a very grave objection, and has prevented any extensive adoption of this method of washing the crystals of sulphate with water.

There are several patented methods for getting rid of the free acid by neutralising it. In one, the salt is exposed to vaporised ammonia, which is caused, by suitable means, to permeate the material. In others, a solid material containing ammonia in some weak combination is mechanically mixed with the sulphate which is to be made neutral, so that the free acid in the latter may combine with the ammonia that is presented to it. These methods of neutralising the free acid by means of added

ammonia, in one form or another, are quite efficient if properly carried out; but they are necessarily more or less expensive, seeing that the ingredient which is introduced into the sulphate must be brought into intimate contact with the latter, necessitating very careful mixture of the materials. Neutralised sulphate is said to be liable to become discoloured; and this is easily understood. For if an excess of ammonia be present in the material it will precipitate, as oxide, the trace of iron which exists in practically all commercial sulphuric acid.

We have now to describe a method which, by the introduction of a simple modification of the ordinary working arrangement, eliminates free acid from the resulting sulphate at practically no expense. This is the process devised by Mr. J. T. Sheard, the chief chemist to the Sheffield Gas Company, whose complete specification has just been accepted by the Patent Office. The process is based upon a realisation of the fact already alluded to, that every crystal of sulphate of ammonia, as it is removed or delivered from the saturator, is enveloped in a film of sulphuric acid, which in the ordinary course is too viscid to flow completely from off the surface of the salt. If, now, this film of acid can be diluted with water, so as sufficiently to reduce its viscosity, it will be enabled to flow away from the salt, leaving the latter practically neutral. In this process, therefore, the mass or magma of crystals enveloped in mother-liquor and acid, is surrounded by a fine mist or cloud of water, immediately it leaves the saturator, and before the mother-liquor has been allowed to drain away from it. The acid film enveloping the crystals of sulphate has a great avidity for water, which it absorbs, and is diluted by, while the salt is protected from meeting with the water, and so is not dissolved; for the water does not come directly into contact with the salt itself. The diluted mother-liquor, which drains away from the salt, carrying with it the free acid, flows back into the saturator. It might be thought that this would lead to too great weakening of the saturator bath; but this is not so. It is duly allowed for. In the ordinary way of working a supply of water, equal to 112 gallons per ton of sulphate made, must be provided, in some form or other, in order to reduce the strength of the acid employed—namely, 140° to 80° Twaddel, which is that generally considered the most useful. By the arrangement described, so much of the water as is necessary is used to dilute the acid on the surface of the salt removed from the saturator, before it enters the saturator itself.—*Gas Journal*, April 29, 1919.

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Continued from p. 225).

"THERE is still another point which calls for attention. If the yellow colour of a liquid is due to the suspension of a certain number of solid or liquid particles, the colour should dissapear as the particles sink; it should be ephemeral. If this were true, the suggested explanation of the different colours of natural waters would present a real difficulty; but this is not the case. I have allowed a turbid lime-water solution to stand for seventeen days in the observation tubes. At first no light came through, but after some time the lime began to precipitate in the tube, and the liquid became more and more green. At the end of twelve days the water was so clear that one could see through the tube a light pencil mark on a piece of paper. The colour of the water was green, nevertheless, and remained so. It was evident that I was dealing with a solution of lime in water without any real suspension of solid matter, and yet there was enough yellow left to form a green with the blue of the water. Turbid waters containing bicarbonate of calcium or of barium in suspension show the same phenomenon, whence it follows that the resistance to the passage of light manifests itself also when light passes through saturated solutions where a precipitate is ready to form. This last might be called a nascent precipitate by analogy with the nascent clouds which Tyndall has taught us to recognise. To test this point experimentally, I have made at 18° a nearly saturated solution of pure calcium chloride containing no iron. In the observation tube this solution was a beautiful greenish-yellow. When diluted with water or when the thickness of the layer was decreased, the green became more marked. An almost saturated solution of pure magnesium chloride has shown a very pure golden yellow. A saturated solution of equally pure sodium chloride was wonderfully transparent and had a magnificent chrome-green colour. I have not examined solutions of other salts because of the difficulty of getting them really free from iron. I believe nevertheless that it is proved that the yellow colour produced by dissolving a salt depends less on the amount of salt dissolved than on the nearness of the solution to the crystallisation point. Small amounts of a slightly soluble salt will produce the same effect as large amounts of a more soluble substance. To test this directly, I boiled pure, blue, distilled water for some time in a glass flask. It is known that glass is slightly soluble in water. When the cooled water was poured into the observation tube, it proved to be completely opaque. After some hours a deep yellow light passed, and at the end of two days it became green and remained so. Its clearness was then very great, but the small amount of transparent material which had been taken from the glass was enough to colour it green.

"We can now show how the observed facts may be used to account for the colours of natural waters. We start with the assumption that a sufficiently thick layer of absolutely pure water has a beautiful blue colour. If small amounts of colourless salts are in true solution, the colour of the water will remain blue; but if the water contains greater or lesser amounts of a nascent precipitate the light passing through the water will be a more or less deep yellow. There may even come a point at which no light will pass and the liquid will appear opaque; in other words, black. The yellow light will necessarily blend with the blue of the water to form a series of tints which will vary with the amount of yellow from greenish-blue through bluish-green to green. If there is too much yellow, the blue will disappear and the water will be a brown yellow or even darker.

"Let us see now how these conditions may be realised in nature. The sparingly soluble substances in the natural waters, which may appear as nascent precipitates, are for the most part calcium carbonate, magnesium carbonate, silica, aluminium silicate or alumina. It is not necessary to consider the more soluble substances such as the chlorides and sulphates of sodium and magnesium because they do not occur in sufficient quantities to produce the effects in question. A blue water like the Lake of Geneva, or, better, like the Lake of Achen in the Tyrol, must have the calcareous matter more completely dissolved the more blue the water is. There must therefore be a sufficient amount of carbon dioxide to form calcium bicarbonate. A green water, on the other hand, like that of the Lake of Constance, must have the calcareous matter in a less perfect state of solution, which must be due to there being relatively less carbon dioxide in the water. It is interesting to note that these predictions are verified. In 1848 Sainte-Claire Deville analysed the green water of the Rhine at Strassburg and the blue waters of the Rhone at Geneva, determining also the dissolved carbon dioxide. (It is surprising that these two analyses are the only ones given in the chemical literature. Are there no others?). The data which interest us are given in Table IV. When referred to a constant quantity of calcium carbonate there is nearly relatively twice as much carbonic dioxide in the

* From the *Journal of the Franklin Institute* clxxxvii., No 3.

waters of the Rhone as in those of the Rhine. The calcareous matter is therefore dissolved more completely in the former case and, as a matter of fact, the waters of the Rhone are blue.

"If it is true that, when other things are equal, a calcareous water is more blue the more completely the calcareous matter is dissolved, it ought to be possible to make a blue water green by bringing it in contact with lime-stone. The free carbon dioxide would then be converted completely into calcium bicarbonate. In the Lake of Achen the water is a deep blue out in the lake and a most beautiful chrome-green along the northern shore where the water is shallow and the bottom consists of lime-stone pebbles from which the waves grind off invisible particles of calcium carbonate, thus causing a change of colour. The greenish tones of shoals at sea and along the edges of lakes are probably due to the same thing. The sands of the sea contain fragments of crushed shells, and the lands along the shores of the lakes are usually sufficiently calcareous to saturate part of the carbon dioxide in the water.

Table IV.—(*p.p.m.*).

	Rhine.	Rhone.
Calcium carbonate ..	135·6	78·9
Free carbon dioxide ..	7·6	7·95

"So far we have considered only the calcareous matter; but silica and alumina can produce the same effect. A green water might contain no trace of calcareous matter, in which case the silica or alumina would have to produce the colour. Would a water containing alumina and silica give different tints and would it be possible to remove the alumina in any simple and natural way? The answer to this is easy. We know that clay or aluminium silicate forms a pseudo-solution in water though not soluble in the true sense of the word. The water of a river flowing over a fat, clayey mud, does not become completely clear on standing. Although the clay is not dissolved, it acts as though emulsified in the liquid. If one adds to the water a solution of a salt, such as sodium chloride, the aluminium silicate precipitates rapidly. This may be observed on an enormous scale at the mouths of large rivers. Their waters remain turbid even though the current has almost disappeared, so long as they do not mix with the sea-water. When this happens, the mud settles rapidly, and this accounts for the formation of those deltas which are built up grain by grain and yet finally dam the river which formed them and force it to change its course. When the alumina precipitates the water becomes blue again Reference has been made to the observations of Schleinitz on board the *Gazelle* as to the sudden changes in the colour of the sea. He noticed that there was an increase in the density of the water when the blue colour reappeared and he therefore concluded that the blue colour was due to the salt. The real explanation is that the salt precipitates the aluminium silicate, which had caused the green colour when present in suspension in the water.

"One other point may be raised. Is it not possible that the polarisation of the light observed by Hagenbach and by Soret in the Swiss lakes was due to the reflections which produce the yellow colour rather than to reflections producing the blue colour?"

While denying that suspended particles are the cause of the blue colour of water, Spring (*Bull. Acad. Roy. Belg.*, [3], 1886, xii., 814) recognises the important part which they play in the colour phenomena.

"One might think that the blue colour of water would be sufficient in itself to account for the blue colour of the Atlantic, the Mediterranean, and certain lakes; but this is not so. The action of water on the different components of white light varies very much. It absorbs the red strongly even in thin layers but it absorbs the other colours to some extent. If one were to examine the solar spectrum after sunlight has passed through an ever-increasing thickness of pure water, one would find the red, the orange, the yellow, and the green disappearing successively and finally the blue when the thickness of the layer was sufficient. The light of the sun would therefore be absorbed completely in absolutely pure water if the water were deep enough. Such water would therefore appear as black as ink. Can such a depth of water be realised in nature? Some years ago Fol and Sarasin (*Comptes Rendus*, 1885, c., 991) made some new experiments to complete work begun by Fol and others, in which they showed that daylight does not penetrate more than two hundred metres into the waters of the Lake of Geneva even in calm weather and in the month of August. They proved this by lowering to different depths in the lake a special apparatus containing photographic dry plates with a rapid bromide emulsion made by our countryman Van Monckhoven. Those plates which were lowered 237—300 metres showed no effect of light when developed, whereas at 170 metres the illumination was apparently about equivalent to that on a clear but moonless night.

"Depths of more than two hundred metres are the rule not only in the ocean but also in most lakes. Consequently these deep waters, from which the light should never return, ought to appear absolutely black to us. Their surface might send back some reflected rays just as ink will; but the mass of the liquid ought not to appear coloured if it sends back no light. Along the shores and in the shallows the blue colour might show because the conditions would be more or less favourable for the daylight being reflected to the eye. The real phenomenon is quite different. The deepest waters are the bluest, and in the shallow waters the blue gives way to green or even to yellowish green and brown. How are we to account for this?

"Tyndall has shown that no natural water is optically empty. Even after standing a long time the water of the Mediterranean and that of the Lake of Geneva scatters a beam of light. We therefore see the natural blue of certain seas and certain lakes because the daylight does not penetrate far enough into them to be absorbed completely. It encounters myriads of particles of foreign substances which reflect it in all directions like a multitude of microscopic mirrors. The effect to the observer is the same as though he were looking through a very thick layer. From this it follows that in a very deep and very clear lake containing relatively few suspended particles, a beam of light would penetrate further than into a more turbid water before all the rays would be reflected back. This clearer water would be a deeper blue and we find actually that the dark blue waters emit less light. It is also easy to explain the variations in the quality and intensity of these waters with sky changes or with varying agitation of the surface. . . .

"If the suspended particles are relatively numerous, a beam of incident light will not be reflected often in the water before melting the particle which will send it out. The blue will therefore not be saturated and will contain much white light. If the particles are few and far between, the beam will pass through a longer route in the water and the effect will be the same as though the observer were looking through a greater thickness. The blue will be more saturated and a deeper shade. In consequence of these multiple reflections the apparent illumination of the water does not necessarily come from a very great depth. The phenomenon is like that observed by all tourists in the mountains who have crossed freshly-fallen fields of snow consisting of the original small crystals which have not yet agglomerated to larger grains. Each hole made by sinking the point of the ice-axe in this snow is illuminated by the most beautiful blue light. This blue does not come from the depths of the ice or the snow, but is due to the fact that a ray of white light has been reflected a million times more or less from the surfaces of the little snow crystals before reaching the eye of the tourist. At each one of these reflections from a blue substance it has lost some of the reddish light and consequently appears more and more blue. This explains why the waters of some mountain torrents are a beautiful blue-

the intensity of which seems out of proportion to the depth of the water. The Ticino gives a series of illustrations of this between Airolo and Bellinzona. This explains why a light object, like an oar for instance, appears blue when plunged a little way into the water of a blue lake, even though the layer of water covering it is not itself sufficient to show the blue. The light reflected back by the object has not only traversed the slight depth between it and the surface, but comes also by reflection from the sides and is therefore blue.

"If the lateral distances are not sufficient, as is often the case near the shores of a lake or a sea, the phenomenon becomes complicated. The light coming from these points will necessarily be less saturated with blue even though the bottom is white. Since water absorbs most readily the least refrangible or red rays, and then the others less and less completely up to the blue rays, the less refrangible rays will not be cut off in a thin layer of water and the light will appear green. This is probably the reason that the waves of the blue sea appear green. One really sees them by light transmitted through a relatively thin layer."

In a later paper Spring (*Bull. Acad. Roy. Belg.* [3], 1896, xxxi., 94, 256) points out that an optically empty water may appear blue when seen from above if the temperature of the liquid is not homogeneous. A column of water unequally heated is equivalent to a light fog if the tube is short and to a dense black cloud if the tube is long enough. "The light is reflected and refracted from the layers of unequal density and is scattered irregularly in all directions as though the liquid contained infinitely small particles. In other words, such a medium does not behave like an optically empty one. This is important for the illumination of clear natural waters. A lake of pure water will appear blue if there are convection currents in it. The presence of solid particles is not absolutely necessary. If the convection currents are infrequent the lake will appear much darker, even though there has been no change in the chemical composition of the water. This is true experimentally. Forel (*Arch. Sci. Phys. Nat.*, 1877, lix.) points out that the soft water lakes are more transparent in winter than in summer. This is because in summer there is a greater difference between the temperatures at the surface and in the depths. In consequence of agitation due to many causes, the layers of water of different density do not remain stratified one above the other in a regular manner. They mix and convection currents are produced in all sorts of directions scattering the light every which way. Forel has observed that during the summer months it is absolutely impossible to see the bottom and to detect the ancient objects which one looks for in the ruins of the lacustrine cities at depths of 3–6 metres. In the winter the water is usually transparent enough to make the search profitable."

Special experiments showed that in a tube twenty-six metres long a difference of 0·57 between the water in the tube and the surrounding medium is enough to produce opacity. "This slight difference is quite within the order of temperature variations which must occur inevitably in the waters of lakes and seas. It makes us see that the tint cannot be the same in the zones exposed to the sun's rays and in the zones situated in the shadow of a cloud or a mountain. The water which receives the rays of the sun must appear more luminous not merely because of the greater amount of light which falls upon it but also because the solar energy makes the water less transparent than that in the shade. If the wind blows unevenly over the surface of the water, differences of the same order may be noted. The wind causes evaporation which lowers the temperature of the water, thus neutralising the convection currents due to the heating by the sun's rays, and making the water appear more transparent, or less illuminated. This accounts for the difference in tints to be noticed on the surface of lakes and seas, differences which indicate to some extent the direction of the wind."

(To be continued).

BOARD OF TRADE ANNOUNCEMENTS.

Standard for the Measurement of Electricity.

The Board of Trade announce that the coils and instruments referred to in the Schedule to the Order in Council of January 10, 1910, which approved the several denominations of standards set out in that Schedule as denominations of standards for the measurement of electricity will on and after May 8, 1919, be deposited at the National Physical Laboratory, Teddington, Middlesex, instead of at the Board of Trade, Standardising Laboratory, 8, Richmond Terrace, Whitehall, London. All communications respecting Electrical Standards and instruments for test should on and after May 8, 1919, be sent to the Director of the National Physical Laboratory, Teddington, Middlesex.

Supply of Goods to the Rhine Territories.

The Board of Trade have extended their General Licence authorising, on certain conditions, the supply of goods to the territories on the left bank of the Rhine in the occupation of the Armies of the Associated Governments, so as to cover, on the same conditions, the supply of goods to the occupied districts on the right bank. As regards both banks of the Rhine, applications should be made to the Export Licence Department, 4, Central Buildings, Westminster, S.W. 1, in respect of goods remaining on Section "A" or "B" of the Prohibited List which it is desired to despatch to the occupied areas (including Luxembourg). Goods on Section "C" of the Prohibited List do not now require a licence for export to the above-mentioned territory, provided in the case of shipment *via* Holland, they are first consigned to the Standard Bank of South Africa, Rotterdam. Goods on the "free" list may continue to be exported free of all restrictions. No import Permit from the Authorities in the occupied areas is now necessary, and the Notice on page 457 of the *Board of Trade Journal* of April 3, 1919, is therefore cancelled.

Dye Industry

The Board of Trade desire to give notice that, in accordance with the procedure laid down in the White Paper (No. Cd. 9194) setting out the scheme for affording State Assistance to the Dye Industry, the Trade and Licensing Committee have nominated the following gentlemen as the Licensing Sub-Committee to deal with all questions relating to the administration of the Prohibition of Import (No. 29) Proclamation, 1919, prohibiting the import of dyestuffs, &c., into the United Kingdom, viz., Mr. W. E. Kay (Calico Printers' Association, Ltd.); Dr. A. Ree (Association of British Chemical Manufacturers); Mr. J. Turner (British Dyes, Ltd.); Mr. Thorp Whitaker (Bradford Dyers Association, Ltd.). The Chairman of the Trade and Licensing Committee (Lord Colwyn) is also the Chairman of the Licensing Sub-Committee. The offices of the Licensing Sub-Committee are at Danlee Buildings, 53, Spring Gardens, Manchester, and any communications should be addressed to the Secretary (Mr. W. Graham) at that address.

Import Restrictions.

The President of the Board of Trade, after duly considering the recommendations of the Consultative Council on Imports, has given the following further directions in regard to the Prohibitions of Import:—The restrictions on the importation of the following goods are to be removed:—

104. Bronze powder.
105. Waste or Scrap Rubber.
143. Glassware (including bottles and jars) other than scientific glass and glassware, machinery glass and glassware, machinery glass and glassware, optical glass and manufactures thereof, mineral lamp glasses, and miners' electric lamps are to be admitted a the rate of 50 per cent of 1913 imports.

Applications for special licences should be made as usual to the Department of Import Restrictions, 22, Carlisle Place, London, S.W. 1.

Flax Control Board.

The responsibility for the Flax Control Board has, by a decision of the Cabinet, been transferred to the Board of Trade as from April 1. The present members of the Board are being invited to continue to act, with the following amended terms of reference:—

"To promote and co-ordinate arrangements, whether by Government Departments or by private enterprise, for the supply and distribution of Flax, Flax Seed, and Flax manufactures for Government aud Civilian purposes and to take such measures as may be necessary in regard thereto."

All communications with regard to the work of the Board should be addressed to Mr. P. Guedalla, Caxton House, Tothill Street, S.W. 1.

Motor Spirit Licences.

On and after May 17, 1919, Motor Spirit may be purchased without the production of a motor spirit licence.

Any holder of a full-duty or half-duty motor spirit licence who has not been supplied with the total amount of motor spirit authorised to be supplied by his licence may apply to the Petrol Control Department for an appropriate repayment of duty, and such application must be accompanied by the licence in respect of which repayment is claimed. Repayment will not be made in respect of loose vouchers.

Applications for repayment should be made as soon as possible after May 16, 1919, and addressed to the Petrol Control Department, 19, Berkeley Street, London, W. 1.

Free of duty motor spirit licences need not be returned to the Department.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 7, 1919.

Dr. Samuel Rideal, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Andrew More, F.I.C.; John Haworth, F.I.C.; and H. T. Lee, M.Sc., A.I.C.

Certificates were read for the second time in favour of Messrs. Charles Frederick Lee Barber, A.I.C.; George Stanley Withers Marlow, B.Sc., F.I.C.; and Frederick William Read.

The following were elected members of the Society:— Messrs. Madanlal Jekisandas Gajjar and James Sorley, F.I.C.

The following papers were read:—

"*The Analysis of Mercury and Zinc Cyanide and of Double Cyanide Gauze.*" By T. F. Harvey, F.I.C., and F. Mackley.

Double cyanide gauze, so extensively used for field dressings during the war, is prepared by impregnating large rolls of gauze with a previously prepared paste containing about 50 per cent of mercury and zinc cyanide. Rapid methods of analysis used by the authors for the control of both paste and finished gauze are described.

"*The Estimation of Small Quantities of Antimony.*" By W. Beam, M.D., F.I.C., and G. A. Freak, B.Sc., F.I.C.

The process is a modification of that proposed by Schidrowitz and Goldsbrough, and consists in depositing the metal on a strip of copper-foil as in the Reinsch test, dissolving the antimony in a boiling alkaline permanganate solution, reduction with sulphur dioxide, and conversion of the antimony into colloidal trisulphide in the presence of gum. Colorimetric comparison is then made with solutions prepared from a standard potassium antimonyl tartrate solution.

"*Studies in Steam Distillation.*" (Part VI.). By H. Droop Richmond, F.I.C.

"*The Detection of Cocaine, Heroine, and Veronal.*" By P. A. Ellis Richards, F.I.C.

ROYAL MICROSCOPICAL SOCIETY.

Ordinary Meeting, April 16, 1919.

Mr. J. E. Barnard, President, in the Chair.

"*Chemistry of Dendritic Growths in Paper.*" By James Strachan.

The formation of these interesting and curious growths was formerly attributed to the oxidation of a particle of bronze or brass included in the sheet of paper during manufacture. Subsequent investigations have proved, however, that the chemical reactions producing these growths are more complex. The particle of bronze is attacked by chemical residues in the paper, chief among which is sulphate of aluminium, with the formation of soluble sulphate of copper. The latter creeps along the fibres in solution. The sulphate of copper is then reduced to insoluble black sulphide of copper, which constitutes the majority of recent dendrites in paper. This sulphide is further oxidised again to sulphate, and so by alternate oxidation and reduction insoluble copper compounds may be deposited along the fibres. The final action in old dendrites is oxidation resulting in the formation of basic copper sulphate. The chemistry of these growths is important in that they indicate, by secondary reactions, the nature of chemical actions taking place in the deterioration of paper during ageing, in which the cellulose is attacked by chemical residues from various sources. A new micro-chemical test for the detection of copper sulphide consists in the application to the dendrite of a solution containing the double cyanide of potassium and cadmium. The black copper sulphide dissolves, but is exactly replaced by a brilliant yellow pseudomorph of cadmium sulphide, forming a yellow dendrite. The principle of this mode of testing by replacement appears to be capable of further applications in micro-chemical manipulation.

"*On* Folliculina boltoni, *S. Kent.*" By Dr. E. Penard.

In spite of recent statements to the contrary, the genus *Folliculina* is undoubtedly represented in fresh water, and the vermiform bodies (described as *Lagynus ocellatus* by Daday) represent, as already suspected by several authors, though contradicted by others, a free-swimming form produced by a metamorphosis of the whole individual.

FARADAY SOCIETY AND RÖNTGEN SOCIETY.

(Joint Meeting).

A joint meeting of the Faraday Society and the Röntgen Society was held at the Rooms of the Royal Society, Burlington House, on Tuesday, April 29, for a discussion upon the "*Examination of Materials by X-rays.*"

Sir Robert Hadfield, F.R.S., opened the discussion, and also read a paper by himself and Messrs. S. A. Main, B.Sc., and J. Brooksbank, B.Sc., dealing with the absorption of X-rays by different kinds of steels and the examination of carbon electrodes used in steel making furnaces.

Prof. Bragg gave a short address on the general principles governing the production of X rays, and many other important papers were read, dealing chiefly with the

examination of metal castings and forgings with a view to revealing defects such as cracks, blow-holes, &c.

A paper by Major G. W. C. Kaye (ex-President of the Röntgen Society) attracted great attention. The subject was the examination of timber by X-rays, and many photographs were shown of the woodwork of aeroplane construction, and many unsuspected serious defects came to light. This method of examination has been of very great value during the war.

Other valuable papers were contributed, of which we hope to give an account in a later issue.

FIFTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES, CHICAGO.

During the week of September 23 to 27, inclusive, there will be given in the Coliseum and First Regiment Armory in Chicago, United States of America, the Fifth National Exposition of Chemical Industries. This is the fifth annual exposition, the four previous ones having been given at the Grand Central Palace in New York.

The Advisory Committee and the management of the Exposition extend to all the chemists of Great Britain, and manufacturers whose industries are based upon the chemical science as well as those interested in chemistry are invited to attend the Exposition. To visitors from this country they extend every facility and courtesy. They advise that there are in Chicago, a city which is a great metropolitan centre, and at the same time a great railroad centre, ample and comfortable as well as pleasant hotel accommodations.

The Advisory Committe of the Exposition is composed of :—Charles H. Herty, Chairman, Editor *Journal of Industrial and Engineering Chemistry* ; Raymond F. Bacon, Director, Mellon Institute ; L. H. Baekeland, Member Naval Consulting Board ; W. D. Bancroft, President American Electrochemical Society ; Henry B. Faber, Industrial Filtration Corporation ; Ellwood Hendrick, President the Chemists' Club ; Bernard C. Hesse, Chemist, General Chemical Co. ; A. D. Little, President Arthur D. Little Inc. ; Wm. H. Nicholas, President American Chemical Society ; R. P. Perry, Vice-President the Barrett Co. ; H. C. Parmelee, Editor *Chemical and Metallurgical Engineering* ; G. W. Thompson, President American Institute of Chemical Engineers ; T. B. Wagner, United States Food Products Corporation ; M. C. Whitaker, President U.S. Industrial Chemical Co. ; and Charles F. Roth and Fred W. Payne. There is also added a special Chicago committee consisting of L. V. Redman, W. D. Richardson, A. V. H. More, Carl S. Minor, F. W. Willard, and Wm. Hoskins ; the managers are Charles F. Roth and Fred W. Payne, and the general office is at 417, South Dearborn Street, Chicago, Ills., U.S.A.

Speaking of the National Exposition of Chemical Industries they say that in the war preparedness of America the part performed by this Exposition was considerable. It was organised in the early days of the great war when America felt so greatly the need of chemicals in the form of dyes, medicinals, industrial chemicals and machinery, and equipment of all kinds. It took an active interest in the natural resources of the country, gathering together specimen exhibits of what the country contained, and brought to its halls the captains of industry and finance, out of the meeting of which with the raw materials and machinery that were shown came those great plants to manufacture the finished products that took so active a part in America's war programme as well as well as her domestic industries. Thus the Exposition has been the stimulus of the remarkable period of chemical development in America ; the serious shortages in medicinals and dyestuffs have been rapidly made good, textiles have been improved, food preservation put upon a better basis, the field of electro-chemistry expanded, the metallurgical industries enlarged, and the manufacture of machinery, apparatus, and innumerable pieces of equipment, both for plant and laboratory, promoted and forwarded. The policy of the Exposition has been uniformly the serious task of enriching the country through the chemical industries, and has never sought popular favour by frivolous display or attractions.

America so well provided in her own industry holds and shows in this Exposition much of value and interest to British industry. With each succeeding year the practice has steadily grown among the exhibitors of withholding until Exposition week any new improvements or products developed during the year. All such recent developments made because of the exigencies of the war will have their public inception this September, and it is fair to predict that many things of exceptional interest will be shown ; there is already an intimation from some sources that numerous new things will be released. The exhibitors' displays are always accompanied by the best technical men from the plants, who devote their entire time during the week to discussions of important technical details connected with the construction of plants, the installation and use of machinery on display, or the application and purposes o the numerous products without which the chemical and dependent industry would be at great disadvantage.

Of machinery, the displays consist of actual operating exhibits working upon materials and under conditions such as are found in any plant, and such operations on a large scale as cannot be shown are explained and carried before visitors by pictures in motion.

During the week of the Exposition there will be held, in the Exposition Buildings, annual meetings of the American Institute of Mining Engineers, the American Electrochemical Society, the American Ceramic Society, the Technical Association of the Pulp and Paper Industry, and the American Chemical Society is co-operating with the Exposition.

The previous Expositions have had an attendance of over a hundred thousand persons interested in the Exposition, with visitors coming from every point in the world. The present indication of the interest of scientific and business men in the Exposition, as evidenced by their interest in the society meetings just held, is expected to be a record-breaking attendance.

At this preliminary writing there are already 279 names on the register of exhibitors, nearly as great a number as at last year's Exposition.

While the programme of the Exposition is not yet announced there is every indication that it will be an exceedingly interesting and engaging one, and the whole Exposition as great a stimulus as during the early war period when its influence was so greatly needed.

NOTES.

New Kaolin Deposits.—New strata of kaolin have been discovered in the island of Börnholm. Temporary investigations indicate that the deposits are rich and that the quality is of the very best.—(*Berlingske T.*, Mar. 20.m., 1919).—*Technical Supplement.*

Benzole Motor Spirit.—In view of the increasing demand for benzole as a motor fuel the Commercial Motor Users Association (Inc.) has just issued a list of suppliers of benzole motor spirit throughout the country. The list, which has been compiled by Capt. F. G. Bristow, General Secretary of the Association, in conjunction with the National Benzole Association, is arranged in counties, and gives the name of the town, the address of the depot, and the hours during which benzole may be obtained. A copy of the list may be obtained, free of charge, on application to Capt. F. G. Bristow, General Secretary, Commercial Motor Users Association, 83, Pall Mall, London, S.W. 1.

The War and Molybdenum.—The war had a marked effect in stimulating the production of molybdenum. On the outbreak of hostilities the price of molybdenite suddenly rose, and in a remarkable degree, the reason apparently being that Germany, aware of the impossibility of laying up enough tungsten, was buying molybdenite to take its place. During the war both England and France found themselves short of tungsten, and they, too, had recourse to molybdenum in the production of high-speed steels. The French used molybdenum in the breech-blocks of some of their field guns, but never, it appears, in shells, armour-plate, or gun-linings. Later in the war it was proposed to make armour-plate containing molybdenum, and contracts were entered into in America to produce such plate. Steel companies were parties to large contracts for molybdenum; but before the steel was actually put to use the war ended. One of the companies concerned used molybdenum, to the extent of less than 1 per cent, in making crank-shafts and connecting rods for Liberty motors.—(*Engineering and Mining Journal*, March 15, 1919).—*Technical Supplement*.

German Iron Industry without "Minette" Ore.—The loss of the Briey Basin, with its immense deposits of rich iron ore, locally known as "Minette," is a staggering blow to the iron industry of West Germany. Germany has in recent years built up a great iron and steel industry, of which the principal centre is the Rhenish-Westphalian districts. It is affirmed that on that industry one-tenth of the population of Germany subsists. But the home production of ore has not kept pace with the output of finished iron, so that more than half of the requirements of the blast-furnaces has had to be imported, many foreign sources having been drawn upon. The ending of the war, so disastrous for Germany, has shaken this great industry to its foundations. The minette of Lorraine is henceforth unavailable. What this means to the industry of the Rhineland will be understood if we consider the fact that out of the 28·6 million tons of ore used in 1913, 21 million tons came to the works from Lorraine. France, which before the war was rich in iron ore, is now likely to become the richest in Europe, thanks in large part, the writer adds, to German intelligence and enterprise. For since 1870 the minette deposits have been brought into their present productive state under German management. German manufacturers must, therefore, set themselves to work the poorer ores of the country and carefully conserve all scrap.—(*Chemiker-Zeitung*, March 12, 1919).—*Technical Supplement*.

Dye-stuffs.—Dominion Products.—In accordance with the policy of removing as far as possible restriction on the import of goods from the Dominions, the Trade and Licensing Committee have issued a general licence covering the importation into the United Kingdom of dye-stuffs, and other products covered by the Prohibition of Import (No. 29) Proclamation, which are of bona-fide Dominion origin. The Prohibition referred to was given in the issues of the *Journal* of February 27 and March 6.—*Board of Trade Journal*.

Benzol for the Dye Industry.—The Board of Trade desire to draw the attention of dye manufacturing firms to the fact that they are in a position to supply quantities of pure benzol for dye making purposes delivered ex-storage tank at various centres at 1s. 9d. per gallon. As the supply is limited, it is desirable that inquiries, even if for forward delivery, should be made at once. All orders should be addressed to the Commissioner for Dyes, Board of Trade, 7, Whitehall Gardens, London, S.W. 1. —*Board of Trade Journal*.

Withdrawal of the Black Lists.—The Foreign Trade Department of the Foreign Office announce that the Allied and Associated Governments have decided that after midnight, April 28—29, all Black Lists of firms and persons which they have published or compiled shall be withdrawn, and that all disabilities attaching to trade and communication with firms or persons on such lists shall cease to operate. The Allied and Associated Governments reserve the right to reintroduce all or any of such Black Lists should such action become necessary.—*Board of Trade Journal*.

Bites of Rabid Dogs.—The Local Government Board has issued a memorandum regarding the steps to be taken by persons who are bitten by dogs suspected to be rabid. The first part is especially interesting to chemists. The memorandum states:—The wound should be treated as soon as possible with undiluted carbolic acid, or with undiluted izal or similar disinfectant. The disinfectant should be allowed to come into contact with all parts of the wound, and should then be washed out with water or dilute disinfectant. If no disinfectant of the kind is available the wound should be thoroughly washed and irrigated with hot or cold water. Where it is possible to get the immediate services of a doctor the treatment should be placed in his hands. Persons bitten by stray dogs or by dogs exhibiting unusual behaviour should at once inform the police with a view to the necessary inquiries being made. By arrangement with the Board of Agriculture and Fisheries the names of all persons known to officers of that Department or to the police to have been bitten by dogs suspected of being rabid will be communicated at once to the medical officer of health of the district in which the bitten persons live. The Board of Agriculture have undertaken to advise the Local Government Board whether the symptoms in the dog are sufficiently suspicious to justify anti-rabic treatment before the confirmatory diagnosis is available, and this information will similarly be forwarded to the medical officer of health. In any case a definite decision for purposes of treatment will be available twenty-four to twenty-eight hours after the material for diagnosis from the dog has been received by the Board of Agriculture and Fisheries. When the medical officer of health is satisfied that anti-rabic treatment is essential, and has ascertained that the person bitten is prepared to begin the treatment, he should communicate with Dr. Dudgeon, Department of Pathology, St. Thomas's Hospital, Westminster Bridge, London.

Dry Cell.—French Patent No. 487,645 of A. Heinz describes a form of dry cell that may be stored permanently without deterioration. The positive electrode of manganese dioxide and graphite is enclosed in a tube of zinc, forming the negative electrode. The zinc tube is closed at its end by cardboard caps, and a hole is provided at one end to introduce the electrolyte just before the cell is put into service. The two electrodes are separated by a tube composed of paper mash boiled in a solution of carbonate of soda and then compressed. This tube is provided with a series of vertical slits.—(*Revue Générale de l'Electricité*, March 29, 1919).—*Technical Supplement*

An Appreciation.—When the United States came into the war, we promised, rather too rashly, to produce some 20,000 planes, perphaps in a year, but certainly within two years. We didn't do it. Great Britain made no promises, but what she did, though apparently little known, is far more than we promised to do. At the beginning of the war Great Britain's capacity for manufacturing airplanes was not greater than 100 per year. At the time the armistice was signed she was turning out planes at the rate of 800 a week! In other words, her production possibilities were demonstrated to be in excess of 40,000 planes a year! Think of that, and remember that it is not America, with her limitless resources of men and money and factory and raw material, but the British Isles, with their very much limited man-power, material resource, and steel industry, which not only built the planes but engined them. And then, as do all other fair-minded Americans who get the actual facts, take off your hat and bow in deep respect to a nation we of America are rather too apt to consider slow and old-fashioned in methods when it comes to factory production.—*Scientific American*.

NOTES FROM FOREIGN SOURCES

Polymerisation of Formaldehyde by Alkalis.—C. Mannich.—It has already been shown that when alkalis act on formaldehyde either formic acid and methyl alcohol are formed, or else aldol condensation, resulting in the formation of "formoses," ensues. The author has found that another reaction may occur, namely, the formation of a polymer of formaldehyde, which separates as a white crystalline mass when moderately concentrated alkalis act at the ordinary temperature on 30 per cent formaldehyde solution. The analysis and the properties of the substance show that it is a polymeric formaldehyde. Auerbach and Barschall have already pointed out that when concentrated sulphuric acid acts on formaldehyde solutions four different polyoxymethylenes are obtained. The α- and β-modifications are soluble in sodium sulphite, while the γ and δ forms are insoluble. The α- and β-modifications are distinguished by their crystalline form and by their behaviour when boiled with water; only the α form is readily soluble in water. The polymerisation product obtained by the author so closely resembles α-polyoxymethylene that there can be no doubt that it is identical with it.—*Ber. Deut. Chem. Gesellschaft*, 1919, lii., 160.

New Method of Determining Oxalic Acid.—Hugo Krause.—The method described by the author has the advantages of being very rapidly performed and requiring only simple apparatus. It can usually be carried out directly, since it is not affected by the presence of other organic or inorganic acids. The substance must be used in solid form. The method depends upon the conversion of oxalic acid into carbon monoxide, the volume of which is determined gasometrically. This reaction is well known to be brought about by the action of concentrated sulphuric acid, but it is not as generally known that acetic anhydride produces the same effect with great ease and rapidity, and quite quantitatively. When free oxalic acid is present an amount corresponding to about 0·1—0·3 grm. of oxalic acid is weighed out in a wide test-tube, fitted with inlet and outlet tubes and a small dropping funnel. Carbon dioxide is led in, and the outlet tube is connected with a Schiff's azotometer containing a 50 per cent caustic potash solution. After all the air has been expelled about 5 cc. of acetic anhydride is introduced through the funnel, and the test-tube is immersed in water at 50—60° which is rapidly heated until it boils gently. The volume of the carbon monoxide liberated is determined in the azotometer, and hence its weight is calculated. The method has to be modified somewhat if the oxalic acid is present as oxalate. If the oxalate is soluble in water it is simply dissolved in 15 per cent hydrochloric acid and then evaporated in the test-tube until a damp crystalline mass is obtained, which is treated as before. If insoluble oxalates are present they must be decomposed by using anhydride which contains sulphuric acid. In this last case the accuracy of the result is affected by the presence of malic acid and lactic acid.—*Ber. Deut. Chem. Gesellschaft*, 1919, lii., 426.

Bromfluorpropylethyl Ether and Fluorallylethyl Ether.—F. Swarts.—The substance used for the preparation of these two compounds was the ethyl ether of asymmetric dibromhydrine, obtained by the fixation of two atoms of bromine on allylethyl ether. It is best to work at a low temperature, and to dilute the allyl ethyl ether with an indifferent solvent. When mercurous fluoride acts on the ethyl ether an atom of fluorine displaces one of bromine. The temperature must be kept at 160—170° for a day, and then raised gradually to 200°, and the reaction is complete in two days. During the action hydrofluoric acid and hydrobromic acid are evolved, and a carbonaceous product is left after distillation. A small quantity of the difluorhydrine, $CH_2F—CHF—CH_2—O—C_2H_5$, is also formed. When bromfluorpropylethyl ether is subjected to the action of sodium methylate it loses a molecule of hydrobromic acid, and is transformed into fluorallylethyl ether. It is a very mobile liquid, having an odour resembling that of all the allyl compounds. When oxidised it yields fluoracetic acid, and hence its formula must be—

$$\begin{array}{ccc} CH_2 & & CHF \\ \| & & \| \\ CF & \text{and not} & CH \\ | & & | \\ CH_2OC_2H_5 & & CH_2OC_2H_5 \end{array},$$

which would give acetic acid. The formula of the bromfluorpropylethyl ether must therefore be $CH_2Br—CHF—CH_2—O—C_2H_5$. Fluorallylethyl ether readily combines with bromine, and the dibrom fluorpropylethyl ether obtained can be distilled without undergoing decomposition, which is an example of the effect fluorine has in rendering a compound stable, for the ethyl ether of dibromhydrine cannot be distilled under atmospheric pressure without undergoing decomposition.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 103.

Researches on Mercury Fulminate and some of its Impurities.—Paul Nicolardot and Jean Boudet.—Hyposulphite of ammonium and of sodium are both good solvents for mercury fulminate, and might both be used to test for impurities in the fulminate which are not soluble in them. The authors have systematically studied the action of the two hyposulphites, and of potassium cyanide upon the various impurities which might be present in the fulminate, such as mercurous or mercuric nitrate, mercurous or mercuric oxalate, and metallic mercury. The results show that hyposulphite is superior to cyanide, for the salts of mercury other than the fulminate are transformed by the hyposulphite into insoluble compounds, while under the action of cyanide they may go into solution and may be regarded as fulminate when the mercury is determined by electrolysis. Commercial mercury fulminate may contain a high proportion of impurities, and the authors regard Brounsdon's method of controlling the analysis of fulminate as very useful (Chemical News, 1904, lxxxix., 303). The following method of treating the residues in the manufacture of fulminate is simple and not expensive:—The fulminate contained in the residues is *extracted by a solution of hyposulphite, the solution is separated off, acidified with a little sulphuric acid, and* boiled. All the mercury then separates in the form of insoluble sulphide, which is filtered off. The mercury is recovered by distillation with lime.—*Bull. Soc. Chim. de France*, 1919, xxv xxvi., 119.

Catalytic Dehydrogenation by Nickel in presence of Hydrogen.—Paul Sabatier and Georges Gaudion.—The hydrogenation of benzene hydrocarbons over nickel at a temperature of about 180° gives the corresponding cycloformic hydrocarbons. Thus, pinene yields the dihydride without any accessory reactions. But if the temperature is raised a different reaction occurs. If pinene and hydrogen are led over a column of liquid at about 350—360° a liquid is obtained which is hardly affected by sulphuric acid, but is energetically attacked by a sulpho-nitric mixture. This liquid consists of a mixture of benzene hydrocarbons (cumene and cymene) and a saturated hydrocarbon not attacked by the sulpho-nitric mixture. The density and absence of rotatory power indicate that it is a menthane and not pinene. Thus, hydrogenation and dehydrogenation occur simultaneously, but the presence of hydrogen is indispensable in order that the reaction may take place—without hydrogen a mixture of terpenes is obtained, arising from the isomerisation of pinene by heat, which is facilitated by the presence of nickel. Other compounds besides pinene undergo the same changes. Thus, limonene gives a little saturated hydrocarbon, but nearly all the product is a mixture of cymene and cumene. Camphene gives analogous results, and menthene revert respectively to cymene and benzine. The same reaction has also been applied to oxygen compounds, and cyclohexanol, for example, has provided a regular yield of phenol. This method of dehydrogenation in presence of nickel can advantageously be applied to the production of benzols from terebenthene, while the hydro-

genation' at lower temperatures (about 180—200°) gives only cyclones and formic hydrocarbons.—*Comptes Rendus*, 1919, clxviii., 670).

Utilisation of Glucose and Lævulose by the Higher Plants.—H. Colin.—It is known that the composition of the reducing sugar in the beetroot leaf differs in the lamina and the petiole. The ratio of dextrose to lævulose, often less than one in the leaf parenchyma, increases all along the medial vein and through the petiole. The same phenomenon is observed in chicory leaves and in most leaves with a fleshy petiole, which do not contain any carbohydrate except crystallisable sugar and the products of its hydrolysis; glucose is present in excess over lævulose in tissues which contain no chlorophyll. The etiolated leaves of beetroot, grown in absence of light, showed an excess of glucose, and also the subterranean parts of Jerusalem artichoke and the colourless leaves of chicory. It is simplest to suppose that the dextrose and lævulose migrate with unequal velocities and are utilised at unequal rates. The concentration of the hexoses in the cells is too low to allow of any appreciable difference in the viscosities, and consequently in the rates of diffusion. In these cases the dextrose is consumed less rapidly than the lævulose by the cells, and it is convenient to adopt the hypothesis of Brown and Morris according to which glucose undergoes combustion in the cell in preference to lævulose, which goes to build up the tissues. It is known that respiration is less energetic in the petiole than in the lamina and in etiolated than in green leaves.—*Comptes Rendus*, 1919, clxviii., 697.

Spontaneous Ignition of Mixtures of Air and Ether Vapour.—E. Allaire.—The author has studied the conditions governing the ignition of air and ether vapour, using a special apparatus by means of which the proportions of the two gases could be varied as desired. The apparatus consisted of a force pump driving air into a gas meter, the measured volume of air passing on into a tube in which it was mixed with ether vapour, obtained by the volatilisation of ether from a tube surrounded by a wire electrically heated. The pure ether was measured with a burette. Thus the proportion of ether at 0° and 760 mm. could easily be calculated if the temperature and pressure were known. The gaseous mixture was led into a U-tube, one limb of which was furnished with points like a Vigreux tube and having an opening through which a thermometer could be introduced into the bend. The whole tube was immersed in an oil-bath. Various catalysts, such as oxides of iron, copper, nickel, &c., were tried, but it was found that they had apparently no influence on the phenomenon, and the mixture ignited spontaneously at about 190°, when the amount of ether present was about 1 grm. per litre. The flame was pale blue, and visible only in the dark, and the products obtained were ethyl and methyl aldehydes and carbonic and acetic acids. No reaction took place before ignition occurred. A knowledge of this phenomenon explains the occurrence of accidents in factories and workshops in which ether vapour may spread accidentally in large quantities. It might be possible, by modifying the conditions of the experiment and by using tubes of greater diameter, to bring about ignition at lower temperatures.—*Comptes Rendus*, 1919, clxviii., 729.

Formation of Troostite at a low Temperature in Carbon Steels, and the Influence of the Temperature of Emersion in Interrupted Hardening.—MM. Portevin and Garvin.—The authors have investigated cases of interrupted hardening, or hardening of limited duration, when the specimen was rapidly withdrawn from the hardening water at a temperature which is called the temperature of emersion. They have thus observed the formation of troostite at a much lower temperature than usual, but always with a marked characteristic recalescence. When the rate of hardening is decidedly greater than the critical rate, recalescence is observed at temperatures down to about 450°. If the rate of hardening is lower than the critical rate, recalescence being already produced at a high temperature in the period of rapid cooling, troostite (or perlite) is always found, and the position of the temperature of emersion does not appreciably affect the structure or the hardness.—*Comptes Rendus*, 1919, clxviii., 731.

Spectral Structure of the J-Rays.—R. Ledoux-Lebard and A. Danvillier.—Barkla and Miss White have recently announced the discovery of the existence of a new series of X-rays, obtained by the absorption method with the lightest elements (C, O, and Al) and coming immediately above the K-rays in the scale of frequencies. It is interesting to study their spectral nature, which is possibly simpler than that of the K series, which comprises four monochromatic radiations. The only element which has the smallest atomic number ($N = 5$), and at the same time has physical properties which enable it to be used as anticathode, is boron, and moreover by extrapolation from the results of Barkla its J-rays should fall in the absorption band of silver, so that the study of its rays by the photographic method is specially indicated. The authors have performed this investigation and find that the continuous spectra are very regular, the K discontinuties of bromine and silver being very clear. No ray of wave-length in the neighbourhood of $\lambda = 0.43$ A.U. nor even contained in the interval $1.0 < \lambda > 0.2$ A.U. could be detected, which is a remarkable fact for an element of atomic weight lower than those of the gases of the air. If the J-rays of boron are emitted with an appreciable intensity in proportion to the continuous spectrum they constitute a single ray which coincides with the K discontinuity of silver.—*Comptes Rendus*, 1919, clxviii., 608.

MEETINGS FOR THE WEEK.

Saturday, May 17.

Royal Institution, 3. "Cæsar's Personal Character as seen in his Commentaries," by Dr. J. Wells.

Monday, May 19.

Institute of Metals, 8. (Ninth Annual May Lecture). "Radio-activity," by Prof. A. Soddy.

Royal Geographical Society, 5. "Uses of Geology in War," by Capt. W. B. R. King.

Tuesday, May 20.

Royal Institution, 3. "British Ethnology—The People of Ireland," by Prof. A. Keith.

Institution of Petroleum Technologists, 5.30. "The Chemist and Engineer in relation to the Petroleum Industry," by F. Mollwo Perkin and T. C. Palmer.

Wednesday, May 21.

Royal Society of Arts, 4.30. "Principles of Japanese Design," by Sir Francis Taylor Piggott.

Thursday, May 22.

Royal Society, 4. "Structure of Lysorophus as exposed by Serial Sections," by Prof. W. J. Sollas. "Preliminary Study of the Energy Expenditure and Food Requirements of Women Workers," by O. Rosenhain. "Report on the Metabolism of Female Munition Workers," by M. Greenwood, C. Hodson, and A. E. Tebb.

Institution of Electrical Engineers, 5.30. "Electrical Phenomena occurring in High Atmospheric Levels," by Dr. S. Chapman.

Royal Institution, 3. "Intensive Cultivation," by Prof. F. Keeble.

Friday, May 23.

Royal Institution, 5.30. "Hubert Hastings Parry—His Work and Place among British Composers," by Sir Alexander C. Mackenzie.

Saturday, May 24.

Royal Institution, 3. "Cæsar as a General," by Dr. Wells.

THE CHEMICAL NEWS

Vol. CXVIII., No. 3085.

A METHOD FOR THE VOLUMETRIC ESTIMATION OF SULPHATES.

By A. C. D. Rivett, M.A., D.Sc.

It is possible to estimate sulphates volumetrically by a simple method which, though of limited applicability, is very useful as a works test in suitable solutions. The method depends upon the fact that moist precipitated barium oxalate reacts quantitatively by double decomposition with dissolved sulphates of certain metals to give barium sulphate and the soluble oxalates of these metals. The latter may be titrated in the filtrate with potassium permanganate.

The reaction with barium oxalate is not rapidly completed at ordinary temperature, but provided the amount of sulphate present be not too great, a few minutes boiling will suffice to complete it. This is apparent from the first set of figures (Table I.). To obtain these a known weight (0·476 grm.) of anhydrous sodium sulphate was dissolved in 100 cc. of water, and treated with excess of precipitated barium oxalate under the conditions quoted in the second column. If the mixture had been heated it was then cooled under the tap and made up to 200 cc. exactly. A portion of the solution was run through a filter, and a known volume pipetted off and titrated with decinormal permanganate in the usual manner. An accuracy to 1 part in 200 may be considered satisfactory in view of possible errors in procedure and the fact that the salts used were not of the highest purity.

Table I.

No.	Conditions.	Wt. of Na_2SO_4 found.
1.	Mixture shaken intermittently in the cold for five minutes ..	0·452
2.	Shaken continuously in the cold for five minutes	0·459
3.	Brought to boiling-point	0·469
4.	Boiled for five minutes	0·475
5.	Boiled for ten minutes	0·473
6.	Boiled for fifteen minutes ..	0·474

It appears that five minutes boiling is sufficient to complete the reaction in solutions containing sodium sulphate in amount approximating to half a grm. in 100 cc.

Since precipitated barium oxalate has quite an appreciable solubility in pure water, it is clear that in very dilute solutions of sulphate error will be introduced on this account. This will, however, be the case over only a limited range, for with increase in concentration of sulphate there will be corresponding increase in concentration of sodium (or other) oxalate formed, and the ionic concentration of the negative radicle will be sufficiently great to repress the solubility of barium oxalate below the limit of experimental error. In obtaining the figures given in Table II. the detailed procedure has in every determination been the following:—

An amount of sodium sulphate (gravimetrically standardised against barium sulphate) was weighed and dissolved in 150 cc. of water; precipitated barium oxalate was added as a moist paste in amount equal to about three times that calculated to be necessary; the mixture was boiled for five minutes, cooled under the tap, and made up to exactly 250 cc.; a portion was run through a filter, and a definite volume titrated with decinormal permanganate. An approximate correction, readily determined with sufficient accuracy, was made for the volume occupied in the 250 cc. flask by the solid precipitates. This procedure avoids delay in washing the precipitate.

Table II.

No.	Wt. Na_2SO_4 taken.	Wt. Na_2SO_4 found.	Percentage error.
7.	None	0·021	—
8.	0·0735	0·0818	+11·3
9.	0·214	0·221	+3·3
10.	0·327	0·336	+2·8
11.	0·563	0·569	+1·1
12.	0·760	0·764	+0·5

Taking 1 in 200 as satisfactory accuracy it appears that the solubility of barium oxalate may be neglected only when the solubility with which it is boiled contains more than 0·75 grm. of sodium sulphate in 150 cc.

With amounts above this the results are quite satisfactory, as will be seen from the next series of analyses in Table III.

Table III.

No.	Wt. Na_2SO_4 taken.	Wt. Na_2SO_4 found.	Percentage error.
13.	0·917	0·921	+0·4
14.	1·262	1·263	+0·1
15.	1·326	1·325	−0·1
16.	1·335	1·330	−0·4
17.	1·468	1·467	−0·1
18.	1·719	1·723	+0·2
19.	2·047	2·036	−0·5

If the amount of sodium sulphate exceeds about 2 grms. in the 150 cc. boiled with barium oxalate, the method is just as accurate provided that the time of boiling be increased in order to complete the reaction. This is shown in the three results given in Table IV.

Table IV.

No.	Wt. Na_2SO_4 taken.	Time of boiling.	Wt. Na_2SO_4. found.	Percentage error.
20.	3·079	5 minutes.	3·034	−1·5
21.	5·013	5 minutes.	4·889	−2·5
22.	4·964	25 minutes.	4·949	−0·3

It is therefore advisable in order to save time in a routine works test of a liquor to take an amount containing from 1 to 2 grms. calculated as sodium sulphate, and to boil this with barium oxalate in a volume of 150 cc.

If other salts be present along with sulphates, double decomposition may take place to some extent between them and the barium oxalate, and so lead to high results. This is confirmed by the analyses given in Table V.

Table V.

No.	Wt. Na_2SO_4 taken.	Other salt present.	Wt. Na_2SO_4 found.	Percentage error.
23.	1·326	None	1·325	−0·1
24.	1·326	2 grms. KNO_3 ..	1·324	−0·15
25.	1·326	10 grms. KNO_3 ..	1·345	+1·4
26.	1·326	25 grms. KNO_3 ..	1·400	+5·6
27.	1·326	15 grms. NH_4NO_3	1·396	+5·3
28.	1·326	20 grms. hydrated $Na(C_2H_3O_2)$ ..	1·343	+1·3

In such cases, where the amounts of other salts remain fairly constant (as they would in a works liquor) and are not excessively greater than the sulphate, an empirical constant correction may be introduced with sufficient accuracy.

This volumetric method of estimating sulphates in solution was used with success last year, practically as described and with an empirical correction, in one of H.M.'s factories where it was necessary to determine the sulphate content of liquors containing principally sulphates and nitrates of sodium and ammonium. It is very much more rapid than the gravimetric estimation as barium sulphate, and the analyses given in Table VI. carried out by one of the laboratory testers show the sort of agreement obtained between the two methods.

Table VI.

Volumetric.	Gravimetric.
6·04	6·11
6·11	6·12
6·35	6·37
5·93	5·99
6·36	6·32
6·08	0·05

The limitations of the method are obvious. It is inapplicable in acid solutions, and cannot be used to determine sulphates of metals forming insoluble oxalates or sulphates in presence of salts containing radicles capable of forming insoluble barium salts. The presence of halides is objectionable in preventing accurate titrations with permanganate. There will, however, be many works solutions to which the method may be applied with accuracy and considerable saving of time.

Chemistry Department, University of Melbourne, March 3·, 1919.

DETERMINATION OF PHOSPHORUS IN PHOSPHOR TIN.

By WILLIAM LORD.

The following adaption of Oettel's method for determining phosphorus in phosphor bronze has been applied to samples of commercial phosphor tin containing up to 6 per cent phosphorus and found very accurate and rapid.

A method in which the metal was dissolved in aqua regia, the tin precipitated as sulphide, and the phosphorus determined as $Mg_2P_2O_7$ in the filtrate, was found to be worthless, the bulk of the phosphorus being carried down with the tin sulphide. In one sample containing 2·6 per cent P no trace of the element could be found in the filtrate from the tin sulphide, but on examination of the precipitate the whole of the phosphorus was found.

An attempt was made to determine the phosphorus by oxidising with nitric acid and igniting the $SnO_2+P_2O_5$ with KCN, after filtering through double filter-papers, as in the ordinary determination by Oettel's method, but extremely low results were obtained, through the reducing action of the filter-paper on the P_2O_5 during ignition and the consequent loss of phosphorus.

1 grm. of the finely divided metal is treated in a large porcelain crucible with concentrated HNO_3, and heated on a water-bath until oxidation is complete. This is indicated when nitrous fumes cease to be evolved and a perfectly white residue remains in the crucible, in which no hard metallic particles can be felt with a glass rod.

Oxidation is often very slow if the metal is not in a state of fine division, the larger particles quickly becoming coated with a protective layer of metastannic acid.

The mass is taken to complete dryness and mixed with six times its weight of pure KCN. The crucible is covered and gradually heated to dull redness for fifteen minutes, by which time reduction of tin oxide to metallic tin will be accomplished, together with a quantitative conversion of the phosphoric anhydride to potassium phosphate. Towards the end of the fusion it is quite easy to collect the tin into one globule by imparting a rotary motion to the crucible, and this greatly facilitates the subsequent filtration. When cold the melt is extracted with steam, the crucible being placed upright in a tall beaker, and a jet of steam blown into it from a boiler. A clean paint can fitted with a cork and delivery tube serves well for the purpose. By this means the fusion may be completely extracted in five or six minutes with very little trouble. The button of tin is filtered off, and the filtrate acidulated with HCl, to decompose KCN and KCNO. Considerable HCN is evolved, and this is best performed under a good hood. After boiling to expel HCN a rapid stream of H_2S is led through the hot solution to remove any tin which may have escaped separation previously, and the precipitate filtered off. A little bromine water is added to the filtrate, which is then evaporated to a bulk of 50 cc. and cooled. It is made slightly ammoniacal, and if any precipitate of iron or aluminium hydroxides occurs this should be filtered off, dissolved in HCl, and reprecipitated, the filtrate being added to the main solution. 10 cc. of magnesia mixture are added, and the solution stirred until the formation of crystalline magnesium ammonium phosphate commences, when stirring should be stopped, and 10 cc. of strong ammonia added. It is best to allow complete precipitation by standing overnight in water.

The precipitate is collected on asbestos, in a Gooch crucible, and washed with 2 per cent ammonia containing ammonium nitrate.

After drying in an air-bath, the crucible is heated at gradually increasing temperature, and finally ignited at the back of the muffle, until a perfectly white mass of $Mg_2P_2O_7$ is obtained. This is seldom accomplished if the precipitate is ignited damp. The percentage of phosphorus is computed in the ordinary way from the weight of $Mg_2P_2O_7$ obtained.

The following mixture (Price and Mead, "Technical Brass Analysis") was used for precipitating the phosphorus:—

Ammonium chloride	11 parts
Magnesium chloride	28 parts
Water	130 parts
Ammonia (1 : 1)	70 parts

1 cc. = 0·01 grm. P.

THE COLOUR OF WATER.*

By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry, Cornell University.

(Concluded from p. 250).

"The real colour of ocean water may often be seen when there are breakers. Light, perhaps directly from the sun, may then traverse the crest of the waves and afterwards reach the observer. In my experience such light shows decidedly green. Again, over the screw of the ship a good deal of air is entangled and carried down, thus providing the necessary reflection from under the surface. Here also the colour is green.

"The only places where I have seen the sea look blue in a manner not explicable by reflection of the sky were Aden and Suez. Although the sky was not absolutely overcast, it seemed that part at any rate of the copious, if not very deep, blue was to be attributed to the water. This requires not only that the proper colour of the water should here be blue, but also the presence of suspended matter capable of returning the light, unless indeed the sea bottom itself could serve the purpose.

"The famous grotto at Capri gives an unusually good opportunity of seeing the true colour of the water. Doubtless a great part of the effect is due to the eye being shielded from external glare and so better capable of appreciating the comparatively feeble light which has traversed considerable thicknesses of water. The question was successfully discussed many years ago by Melloni, who remarks that the beauty of the colour varies a good deal with the weather. The light which can penetrate comes from the sky and not directly from the sun. When the day is clear the blueness of the sky co-operates with the blueness of the water.

"That light reflected from the surface of a liquid does not exhibit the absorption colour is exemplified by brown peaty water such as is often met with in Scotland. The sky seen by reflection is as blue as if the water were pure. But an attempt to illustrate this fact by experiment upon quite a small scale was not at first successful. A large white photographic dish containing dark brown oxidised

* From the *Journal of the Franklin Institute* clxxxvii., No. 3.

'pyro' was exposed upon the lawn during a fine day. Although the reflected light certainly came from the clear sky, the colour did not appear pronounced, parly in consequence of the glare of the sunshine from the edges of the dish. The substitution of a dish of glass effected an improvement. But it was when the eye was protected from extraneous light by the hands, or more perfectly by the interposition of a pasteboard tube held close up, that the blue of the reflected light manifested its proper purity. It would seem that the explanation is to be sought in diffusion of light within the lens of the eye, in consequence of which, especially in elderly persons, the whole field is liable to be suffused with any strong light finding access.

"As regards the proper colour of pure water, an early opinion is that of Davy, who, in his *Salmonia*, pronounces in favour of blue, basing his conclusion upon observations of snow and glacier streams. The latter, indeed, are often turbid, but deposit the ground-up rock which they contain when opportunity offers, as in the Lake of Geneva. A like conclusion was later put forward by Bunsen on the basis of laboratory observations. The most elaborate experiments are those of Spring, who, in a series of papers published during many years, discusses the difficult questions involved. He tried columns of great length—up to 26 metres; but even when the distance traversed was only 4 or 5 metres he finds the colour a fine blue only to be compared with the purest sky-blue as seen from a great elevation. But when the tubes contain ordinary water, even ordinary distilled water, the colour is green, or yellow-green, and not blue.

"The conversion of the original blue into green is, of course, explicable if there be the slightest contamination with colouring matter of a yellow character—*i.e.*, strongly absorbent of blue light. Spring shows that this is the effect of minute traces—down to one ten-millionth part—of iron in the ferric state, or of humus. The greenness of many natural waters is thus easily understood. Another question examined by Spring is not without bearing upon our present subject—viz., the presence of suspended matter. I am the better able to appreciate the work of Spring, that many years ago I tried a variety of methods, including distillation *in vacuo*, in order to obtain water in the condition which Tyndall described as 'optically empty,' but I met with no success. Spring has shown that the desired result may be obtained by the formation within the body of the liquid of a gelatinous precipitate of alumina or oxide of iron, by which the fine particles of suspended matter are ultimately caried down.

"Perhaps the most telling observations upon the colour of water are those of Count Aufsess, who measured the actual transmission of light belonging to various parts of the spectrum. The principal absorption is in the red and yellow. In the case of the purest water there was practically no absorption above the line F, and a high degree of transparency in this region was attained even by some natural waters. That these waters should show blue, when *in sufficient thickness*, is a necessary consequence.

"In my own experiments, made before I was acquainted with the work of Aufsess, the light traversed two glass tubes of an aggregate length of about 4 metres (12 feet). On occasion the light was reflected back so as to traverse this length twice over. I must confess that I have never seen a blue answering to Spring's description when the original light was white. For final test I was careful to employ the light of a completely overcast day, which was reflected into the tubes by a small mirror. The colour, after transmission, showed itself very sensitive to the character of the original source. The palest clear sky of English winter's day gave a greatly enhanced blue, while, on the other hand, isolated clouds are usually yellowish, and influence the result in the opposite direction. I should myself describe the best colour of the transmitted light on standard days as a greenish blue, but there is some variation in the use of words, and perhaps in vision. Some of my friends, but not the majority spoke of blue simply, but all were agreed that the blueness of a good sky was not approached. The waters tried have been very various. Sea-water from outside the grotto of Capri, from Suez, and from near the Seven Stones Lightship off the Cornish Coast, I owe to the kindness of friends. Of these the two former showed a greenish-blue, the latter a full, or perhaps rather yellowish, green, and these colours were not appreciably modified after the water had stood in the tubes for weeks. It is important to remember that the hue may to some extent depend upon the thickness. It is quite probable that in a greatly increased thickness the Capri and Suez waters would assume a more decided blue colour. But I do not think the Seven Stones water could so behave, the colour, with 12 feet, seeming to involve the absorption of blue light. Further observations on greater depths of sea-water would be desirable. A naval son informs me that off the coast of Greece a plate lying in six fathoms of water looked decidedly blue, although the sky was a dirty grey. I have doubts whether this would be generally the case in the Mediterranean; the green due to moderate thicknesses seems too decided.

"Of natural fresh waters that I have tried, none were better than that from a spring in my own garden. This water is hard, but bright and clear, and it shows a greenish-blue, barely distinguishable from that of the Capri and Suez water. Distillation does not improve the blue. Neither did other treatments do any good, such, for example, as partial precipitation of the lime with alkali, or passage of ozone with the idea of oxidising humus. Wishing to try water of high chemical purity, I obtained—through the kind offices of Sir J. Dewar—water twice distilled from alkaline permanganate, and condensed in contact with silver, but the colour was no bluer. In the light of this evidence I can hardly avoid the conclusion that the blueness of water in length of 4 metres has been exaggerated, especially by Spring, although I have no reason to doubt that a fully developed blue may be obtained at much greater thicknesses. I should suppose that sufficient care has not been taken to start with white light. It may be recalled that overcast days are not so common in some parts of the world as in England.

"A third possible cause of apparent blueness of the sea must also be mentioned. If a liquid is not absolutely clear, but contains in suspension very minute particles, it will disperse light of a blue character. Although, undoubtly, this cause must operate to some extent, I have seen no reason to think that it is important. But the existence of three possible causes of blueness complicates the interpretation of the phenomena. Hitherto, observers have not been sufficiently upon their guard to distinguish blueness having its origin in the sky from blueness fairly attributable to the water itself."

The question at issue seems to be whether Lord Rayleigh's negative results are to outweigh Spring's positive results. On general principles, there are so many ways of failing in an experiment that a positive result usually outweighs any number of negative ones. On the other hand, Lord Rayleigh is such a careful worker that his conclusions are not to be rejected hastily. The fact that he does not give details to the same extent that Spring does cannot be charged against him because he was delivering an address before the Royal Institution, while Spring was writing a series of scientific papers. The whole question must therefore be considered as open for the present, though one may at least hope that Spring will prove to be right.

Beebe seems to feel that the colour of water is entirely an optical illusion ("Sea-Wrack," *Atlantic Monthly*, 1918, 481). "One finds numerous examples of these sensory deceits at sea. The wind flutters the fins of the flying fish and we think they actually fly. The tropic sea, under the palest of green skies, is saturated ultramarine, save where the propellers churn it to pea-green, yet in our bath the water is clear and colourless. . . . The great unlovely bow rose and reached forward and settled, until

as I lay face-downward our speed seemed increased many-fold. And I wondered if the wooden expression which always marked the figure-head ladies and gods had not its origin in the hypnotic joy of forever watching the molten cobalt crash into alabaster, this into emerald, then to merge again into the blue, which is a hue born of depth and space and not of pigment."

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 248).

The Distillation of Gallium Chloride.

Zinc chloride boils at 730°. Indium trichloride volatilises very slightly at 440° and only slowly at 600°. Gallium trichloride melts at 75·5° and boils at 215—220°. These with a view to ascertaining whether gallium chloride free from zinc and indium might be thus prepared.

A preliminary chlorination and distillation was made with a portion of the original alloy. A glass tube of about 2 cm. diameter was slightly bent in the middle, and a portion of the alloy (3·3962 grms.) was placed in the lowest part of the bent tube. A small oven constructed of asbestos board was placed around this portion of the tube (Dennis, "Gas Analysis," p. 202). Dry chlorine was passed through the tube, and the oven was heated to 240°. Some of the resulting chlorides distilled and condensed in the cold portion of the tube beyond the oven. The spark spectrum of this material showed faint lines of indium and zinc and strong lines of gallium.

An apparatus of the form shown in Fig. 1 was then constructed, the tube A being of Jena glass. About 4 grms. of the alloy was placed in A, dry chlorine was passed into the tube, and the lower end of A was heated to start the

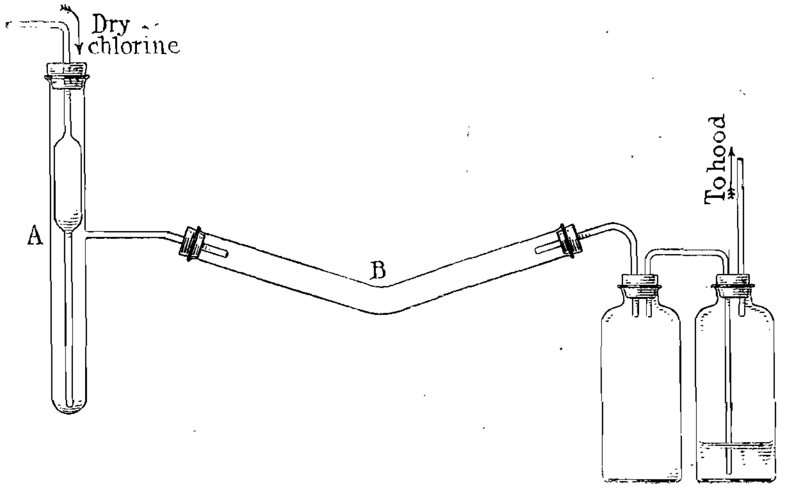


Fig. 1.

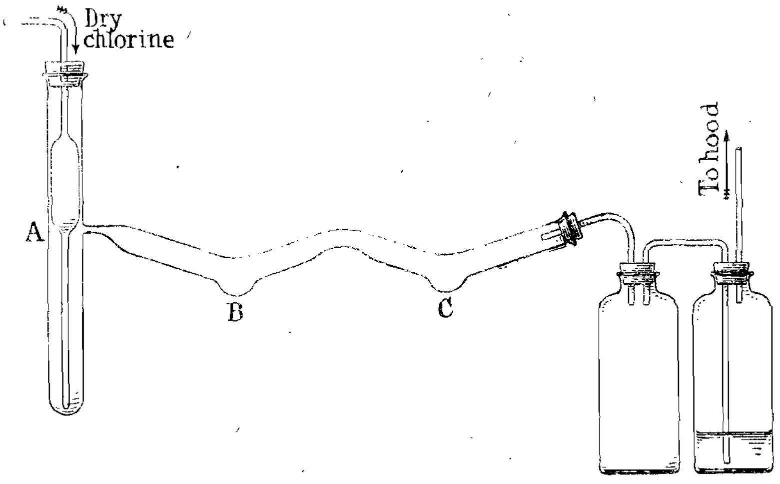


Fig. 2.

facts warranted the study of the fractional distillation of the anhydrous chlorides of zinc, indium, and gallium,

reaction between the alloy and the chlorine. The heat of reaction then suffices to complete the chlorination, and it causes some of the chloride to distil to the upper portion of the tube, nearly to the side-arm. After chlorination was complete a Snowdon electric furnace was brought up around the tube A, and this was then heated to about 230° (*Cornell Chemist*, 1914, iv., 13). This caused a portion

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

of the chlorides to distil over into B. The temperature was raised to 250°, and the distillation was continued for about one hour. The spark spectrum of the material that condensed in B showed the presence of a preponderating amount of gallium, and the lines of indium were only faintly visible. The material remaining in the tube A showed strong lines of gallium, indium, and zinc.

Purified gallium chloride from the tube B (Fig. 1) was again distilled in chlorine, the side-arm for the apparatus in this case being fused to a tube of Jena glass that had two depressions, B C (Fig. 2). Gallium chloride was melted and poured into the tube A. Dry chlorine was passed through the apparatus, and A was heated to from 220—240° in a Snowdon furnace. Gallium chloride that condensed in B was then distilled over into the depression C by heating the tube B with the flame of a Bunsen burner. The spark spectrum of the chloride that condensed in C showed very faintly the α-line of the indium spectrum when a large amount of the material was placed in the spark cup.

The above preliminary experiments gave reason to suppose that several successive distillations of gallium chloride in a current of chlorine would free it from indium and zinc. These distillations were carried out in a tube of Pyrex glass of about 20 mm. external diameter, bent into a series of nine depressions (Fig. 3). The tube was constricted between the depressions. 5·3978 grms. of the original alloy was placed in the first bend A, and dried chlorine was conducted through a glass tube, the end of which dipped below the surface of the alloy. The reaction between the chlorine and alloy was started by heating the latter with a Bunsen flame. The action was at first violent, the union of the chlorine with the metals being accompanied by the emission of a bluish light and a play of incandescent particles throughout the tube in the neighbourhood of the sample. When a layer of the molten chloride had formed above the metal the chlorination proceeded quietly.

After the metals in the alloy had been completely converted to chlorides, the portion of the tube marked A was surrounded by the asbestos oven mentioned above and was heated from 220—250°. A portion of the chlorides distilled over into depression 1. The chloride was successively distilled in this manner from one section to the next until it finally was collected in the last section, No. 8, of the tube. The distillation of the chloride from one depression to the next was effected by slipping over the

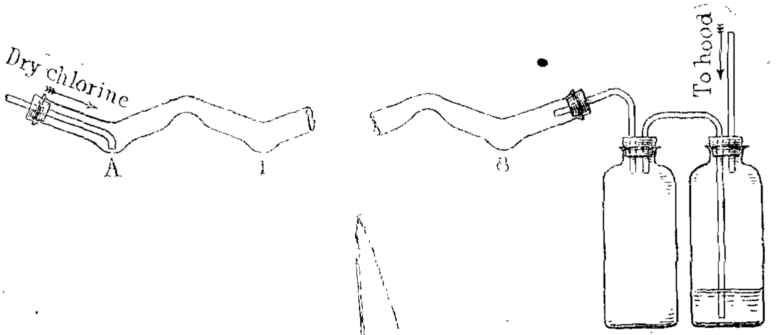


Fig. 3.

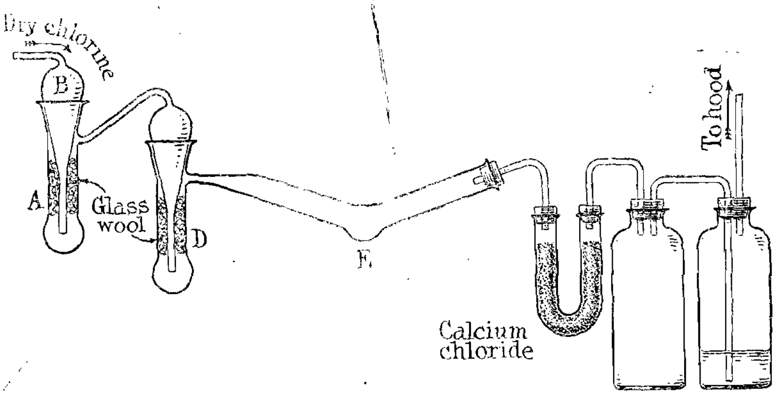


Fig. 4.

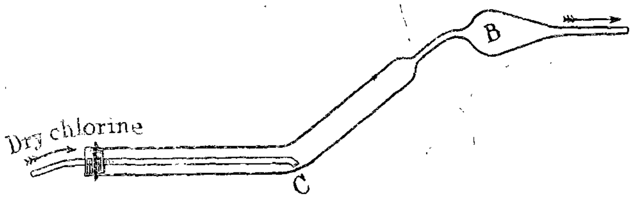


Fig. 5.

glass tube the barrel of a porous cup from which the bottom had been cut off, and which had been wrapped with nichrome ribbon so that it could be electrically heated. This heating tube was about 7 cm. in diameter and 15 cm. long. In distilling the chloride from section 1 to section 2 the heating tube was placed around depression 1, and the current was adjusted to raise the temperature to 254°. In the succeeding distillations the heating tube was moved along until it covered the section containing the chloride and the current was adjusted to give a temperature ranging from 235—245°. A slow current of chlorine was passed through the tube during the distillations. The spark spectrum of the material which condensed in section 8 of the tube, and which consisted chiefly of gallium chloride, still showed faintly the lines of indium and zinc. The indium spectrum was stronger than from the material obtained in the preceding experiment.

The failure to obtain pure gallium chloride by these eight distillations may have been due either to (1) insufficient vertical rise between the different depressions in the distilling tube, which might allow the chlorides of zinc and indium to be carried along mechanically; or to (2) over-heating during the chlorination of the alloy, which might cause either the distillation of some zinc chloride, or the distillation of indium monochloride or indium dichloride before the conversion of the indium to the trichloride was complete; these lower chlorides of indium would first be formed, and they are more volatile than the trichloride.

To remove the first of these possible difficulties an apparatus of different form was constructed (Fig. 4). This was blown entirely of Jena glass, and the tubes A and D were fitted at the top with widened inlet tubes that were ground into the necks of the two distilling tubes. The gallium chloride from the two preceding experiments, which was nearly free from zinc and indium, was melted and poured into the tube A. Glass-wool that had previously been washed with hydrochloric acid and carefully dried was inserted in A and D around the inlet tubes. The chlorides were distilled from A into D in a current of dry chlorine by heating A with a Snowdon furnace from 230—255°. The material that condensed in D showed the lines of neither zinc nor indium. This chloride was removed from D, dissolved in water, and its solution was electrolysed with a rotating rod of platinum as cathode until a small amount of metal was deposited. The spark spectrum of the solution of this deposit in hydrochloric acid showed the lines of neither zinc nor indium.

Because of the success of this method of distillation in freeing gallium chloride from indium and zinc it was decided to convert the large amount of metallic gallium that had been prepared by electrolysis (see *ante*) to the chloride, and to subject this chloride to all distillations. This gallium was nearly free from indium and zinc. The chlorination of the metallic gallium was carried out in the bent tube C (Fig. 5) of Jena glass that was fused to the inlet tube B of the flask A (Fig. 4). Metallic gallium was placed at the depression C and the chlorination was made as described above, B not being connected with A during the procedure. This avoided the possibility of the distillation of zinc chloride and lower chlorides of indium into A and D during the chlorination of the metal. After chlorination was complete the tube B was inserted into the neck of the flask A, and C was warmed to such a temperature as caused the chlorides to melt and flow down into A. The current of chlorine was continued through the apparatus, and A was heated in a Snowdon furnace while the chloride distilled through the glass-wool from A into D. When all of the chlorides had condensed in D the heating of A was discontinued, and the furnace was brought up around the tube D and the chloride was again distilled through the glass-wool into the tube E, where it condensed.

In the first chlorination and double distillation 5·009 grms. of the purified metallic gallium was employed. A slight leakage of the vapour of gallium chloride into the outer air took place through the ground joints at the top of A and D. This was stopped in the next distillation by sealing these joints with water-glass.

A second portion of gallium weighing 9·2982 grms. was chlorinated and distilled, and then a third sample weighing 8·4075 grms. was later chlorinated and distilled.

The residue left in A after the first two samples had been distilled over was tested for the presence of zinc with the microscope, using solid potassium mercuric thiocyanate (Behrens, *Zeit. Anal. Chem.*, 1891, xxx., 141), and zinc was found to be present.

The residue remaining in C where the chlorination was carried on and the chloride that condensed in D gave no test for zinc by this method. This method, however, has been found to be not wholly reliable for the detection of minute amounts of zinc in the presence of large amounts of gallium (Ruth E. Chipman, "The Mercuric Sulphocyanates as Reagents in Microscopic Qualitative Analysis," a thesis presented to the Faculty of the Graduate School of Cornell University, June, 1917).

In an attempt to increase the delicacy of this microscopical test for zinc the gallium chloride was first volatilised at 250° and the test was then applied to the residue, but the results were not successful. The most satisfactory method for determining the purity of the gallium chloride prepared by the above method was found to be the photographing of the arc spectrum of the material (see *ante*). This redistilled gallium chloride was found to be spectroscopically free from zinc and indium, and by the method above described it was shown that it could not contain more than 0·005 per cent of either of these two elements. Two successive distillations of gallium chloride in the apparatus shown in Fig. 3 therefore yield a product of high purity.

(To be continued).

THE ESTIMATION OF PHOSPHORUS IN THE PRESENCE OF TUNGSTEN.*

By G. WATSON GRAY and JAMES SMITH (Liverpool).

In view of the large amount of tungsten used in the manufacture of high-speed steel, the question of the estimation of phosphorus in the presence of tungsten is an important one, but, although important, does not appear to have had the attention it deserves. Judging from numerous analyses which have come under the authors' notice, many chemists seem to find less phosphorus than is actually present. On investigating the cause of some of the low results they were found due to faulty methods. Taking ferro-tungsten as an example, the authors found that the method adopted by many chemists was to decompose the ferro-tungsten by fusion or other methods, separate the tungstic acid by evaporating to dryness with hydrochloric acid, and estimate the phosphorus in the filtrate. This method is altogether wrong, as a large amount of the phosphorus present is precipitated with the tungstic acid as phospho-tungstic acid, and the phosphorus so precipitated is lost. Most ferro-tungstens contain only 0·015 to 0·030 per cent phosphorus, and with these the error is perhaps not quite so glaring, but odd samples made from phosphoric tungsten ores contain up to 0·100 per cent, and sometimes even more. It is in these high phosphoric samples that the error stands out prominently. The authors have seen samples containing 0·100 per cent phosphorus returned as containing 0·020 per cent. To illustrate this point a table of results obtained by using the faulty method described above is given, together with the figures obtained by further examining the residue of tungstic acid for phosphorus. These results are only a few selected from a large number of samples examined.

* A paper read before the Iron and Steel Institute, May 8, 1919.

which took place in private, and at which the statutes of an international confederation, which is to aim at bringing about an intimate alliance between France, England, Belgium, the United States, and Italy, were fixed. An inter-allied council, which is to meet in London on July 15—18, was appointed, each nation appointing two members as follows:—

Belgium—MM. Chavanne and Crismer.
United States—Dr. Cottrell and Lieut.-Col. Zanetti.
France—MM. Moureu and Paul Kestner.
Great Britain—Sir William Pope and Mr. Henry Louis.
Italy—Senator Paterno and M. Parodi-Delfino.
General Secretary—Mr. Jean Gerard.

At the public meetings, which took place on April 14 and 15, communications of the greatest interest were presented. Prof. Louis described modern methods of enriching iron minerals by magnetic separation, and Dr. Cottrell gave an account of the preparation of helium for balloons and dirigibles. A communication on the potash industry in the United States by Mr. MacDowell was also read at the meeting on April 14, and on the following day an exposition of the American patent laws was given by Mr. John Pennie. A banquet was held in the evening, and on the 16th a visit was paid by the members of the Conference to the devastated region of Chauny.

BOARD OF TRADE ANNOUNCEMENTS.

Import Restrictions

The President of the Board of Trade, after duly considering the recommendations of the Consultative Council on Imports, has given the following further directions in regard to the prohibitions of imports:—

The restrictions on the importation of the following articles are to be removed.

201. Printing inks.
202. Oil-lamp burners.
203. Gas-burners.
204. Metal parts and accessories of pedal cycles except those mentioned under No. 225.
205. The following painters' colours and pigments except in so far as they may fall within the scope of the Prohibition of Import (No. 29) Proclamation of February 24, 1919: —Asphaltum; bitumen for black varnish; bone pitch; Brunswick black; burnt sienna; bone black; carbon black; carmine; China ink; Chinese ink; cinnabar native; cobalt oxide; earth colours; earth sienna; gamboge; gamboge gum; Indian ink; imitation gold leaf; lime green; ochre; orpiment; umber; zaffre.
206 Aluminium powder.
207. Fancy goods (articles de Paris).
208. Jewellers' findings; that is, chain, brooch catches, pins and joints, snaps, bolt and split rings of base metal or gilt.
209. Paints and enamels (from July 1).
210. Aerated mineral and table waters.
226. The following painters' colours:—Litharge, ultramarine blue, white lead, satin white, lamp black.
227. Metal fittings and frames for bags and trunks.
228. Raw spirits for industrial purposes.
229. Reclaimed rubber.

In accordance with the above, general licences have been issued for the articles mentioned in items 202 to 206. In the case of printing inks and aerated mineral and table waters general licences are already in operation, and a general licence will be issued in due course for paints and enamels.

Applications for special licences should be made as usual to the Department of Import Restrictions, 22, Carlisle Place, London, S.W. 1.

Export of Foodstuffs to Germany.

The Board of Trade announce that, following on the relaxations recently made in the Blockade regulations relating to foodstuffs whereby:—

(a) The quantitative limitations on the import of foodstuffs into neutral countries have been removed;
(b) Consignment may be made direct to neutral traders, and need no longer be made through the N.O.T. or other importing associations; and
(c) Export from neutral countries to Germany is allowed;

it has been decided to authorise the resumption, by firms in the United Kingdom, of exports of foodstuffs to Germany, through neutral and allied countries, within the monthly ration of foodstuffs allowed to Germany under the Brussels Agreement, and a general licence under the Trading with the Enemy legislation has been issued to give effect to this decision.

All arrangements for finance should be made by, and at the risk of, the private traders and the neutral or allied *firm or Government concerned.*

Foodstuffs on List C of prohibited exports may be exported to Northern Neutrals and Switzerland, as well as to allied countries without licence; but foodstuffs on Lists A and B can be so exported only under licence from the Export Licence Department, 4, Central Buildings, S.W. 1.

The term "Foodstuffs" means food, beverages, spices, edible oils, or other articles intended solely for the manufacture of human food.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 15, 1919.

Sir J. J. Thomson, O.M., President, in the Chair.

The following papers were read:—

"*On the Area of Surfaces.*" By Prof. W. H. Young, F.R.S.

Many attempts by well-known writers have been made to frame a theory of the area of surfaces. These efforts have been attended with so little success that even the most recent text-books define the area of a curved surface by means of the formula known to hold in the case of a surface of revolution. Not even in the matter of the definition itself has anything which can be regarded as final been achieved, still less has it been found feasible to proceed from the definitions which have been given to the formula required.

In the present communication the author attacks the question from an entirely new point of view. The definition given is based on what is itself a new concept, namely, that of the area of a closed skew curve. It is characterised further by the use to which is put the idea that the surface is, like a curve, an ordered manifold, the order being double instead of single.

The surface is accordingly supposed defined by equations of the form—

$$x = x(u, v) \qquad y = y(u, v) \qquad t = t(u, v)$$

and divided up by the curves—

$$u = \text{const.} \qquad v = \text{const.}$$

On the fact that the sum of the areas of the boundaries of the portions of surface thus obtained has a unique limit, the definition of the area of a surface is based. The curve boundaries have in fact an area whenever they possess a length. Moreover, the unique limit obtained for their sum is shown under very general conditions to have precisely the value given by the well-known formula.

It may be added, though this is not proved in the paper, that the theory developed may be utilised to indicate the limitations of the older method, based on triangulation, and at the same time to notably extend such results as have been obtained by earlier writers.

"*On Change of the Independent Variables in a Multiple Integral.*" By Prof. W. H. Young, F.R.S.

"*Researches on the Chemistry of Coal.* Part I. *The Action of Pyridine upon the Coal Substance.*" By Prof. W. A. Bone, F.R.S., and R. J. Sarjant.

The paper records the result of an experimental investigation of the so-called solvent action of pyridine and homologues upon the coal substance, with the double object of clearing up certain discrepancies in the work of previous investigators, and of determining the real nature of the action in question.

It is shown that the presence of oxygen has an important retarding action upon the extraction process (the extent of which varies considerably with the nature of the coal), and that in order to obtain consistent results in any such process, it is necessary not only to employ an anhydrous solvent, but also to exclude oxygen. A suitable apparatus and method are described for carrying out the process under standard conditions, such as will give consistent results of comparative value with various coals.

The application of the method to two typical isomeric bituminous coals is fully described. It is shown that when such extraction is carried out at ordinary pressures, with exclusion of oxygen, a practical limit is finally attained. In the case of the two coals in question, this limit considerably exceeded the amount of "volatiles" yielded by them on carbonisation at 950°. At higher pressures this first limit was considerably passed, and when conducted in sealed tubes between 130° and 150° as much as two-thirds of the coal substance was rendered soluble.

The results as a whole indicate that neither pyridine alone, nor even pyridine in conjunction with chloroform, is capable of extracting in a pure condition the resinic constituents of the coal substance, and that in addition to any ordinary solvent action which pyridine may have upon such constituents it also at the same time slowly attacks and resolves into simpler molecular aggregates the complex structure of the coal substance as a whole, for which it has a marked affinity.

"*A New Method of Weighing Colloidal Particles.*" By Prof. E. F. Burton.

When fine colloidal particles are dragged up and down for equal periods in a liquid by the application of a vertical electrical field a net settling of the particles is noted. It is thought that, although for small forces such as gravity alone the Brownian movement prevents the attainment of any limiting velocity, yet when the particles are dragged by a much larger force the comparatively insignificant gravitational force is added to the electrical for downward motion and subtracted for upward motion, thus becoming effective in producing a net settling of the particles.

Application of Stokes's Law to this net settling gives a value for the size of the particles very closely agreeing with that obtained by the counting method (*e.g.*, $2{\cdot}2 \times 10^{-5}$ cm. and $1{\cdot}7 \times 10^{-5}$ cm.) even though values to hand are taken from old observations made when this net settling was not appreciated and not closely observed.

Experiments are now in hand to determine this settling very exactly. By the application of ultra-microscopic illumination of single particles in a slowly alternating field, it is hoped that the setting will be observed over an extended interval and that a very exact method of weighing these particles will be developed. In addition, the method should prove useful in determining the effect of the addition of various electrolytes on the size of colloidal particles and thereby shed much light on incipient processes of coagulation.

"*The Value of the Rydberg Constant for Spectral Series.*" By W. E. Curtis.

PHYSICAL SOCIETY.

Ordinary Meeting, March 28, 1919.

Prof. C. H. Lees, President, in the Chair.

A discussion on "*Metrology in the Industries*" was held.

Sir Richard Glazebrook, C.B., F.R.S., in opening the discussion, traced briefly the early history of metrology. While in some form or other it must have been employed in the very earliest times—if what antiquarians told us of the Pyramids was correct—the first application of really accurate measurement to mechanical engineering was chiefly due to Sir Joseph Whitworth, who taught people to make their length measurements with great accuracy and introduced reference gauges. The next step was the use of limit gauges. This greatly simplified the gauging of repetition work. At the time of the Boer War the supplies of ammunition, especially breech plugs of guns, were not interchangeable as obtained from different shops. This led to the formation of the Engineering Standards Committee on Gauges, which tackled the problem of producing accurate gauges with defined limits and tolerance, and by 1914 a certain number of firms had introduced the use of limit gauges. In 1915 the cry for munitions on a great scale brought home the great importance of interchangeability and the need for strict standardisation of gauges. When screw gauges were first tested at the National Physical Laboratory the rejections total'ed 75 to 80 per cent; but after two years this was reduced to about 20 per cent. Now, if we are to maintain our position in peace, the maintenance of interchangeability in the engineering manufacture is equally necessary, so that we may manufacture in quantity. Much has yet to be done if we are to keep ahead, and the co-ordination of research with routine testings is vital to the progress of the science.

Mr. Taylor (of Messrs. Taylor, Taylor, and Hobson) agreed that the war had produced a great advancement in the standardisation of manufactures; but we were apt to overlook much that had been done in this way before the war. Interchangeabilty of manufacture had existed, for instance, in the watch trade in Switzerland for centuries. In America, interchangeable manufacture had been introduced by Col. Colt in the Civil War, and was widely practised in America before it was generally understood in this country. But something, nevertheless, had been done in this country. The Linotype Company had done much in this way, while bicycle making had taught us a great deal of interchangeable manufacture. Our schools were at fault in teaching the science of design to the exclusion of the science of the workshop.

Sir Henry Fowler (Chief Mechanical Engineering Department, Midland Railway) said he was sure the country did not realise the debt it owed to the National Physical Laboratory in connection with gauges. While, as Mr. Taylor had said, a certain amount of interchangeable work was done in this country before the war, the country, as a whole, did not appreciate the advantage of limit gauges. A great deal of education is still wanted. To produce economically we must produce in quantity. For this it is essential to have interchangeability, and we can only have this if the science of metrology goes ahead.

Dr. P. E. Shaw (University College, Nottfngham) said he thought the extent to which metrology had now permeated the workshops of the country made decentralisation desirable, and he thought the universities were the proper sites for the subject. He had instituted a department of metrology in University College, Nottingham, in 1916. The instruction would be mainly practical, but preliminary lectures would be necessary as well. In addition to the instruction work testing should be done, the standards used being verified periodically at the National Physical Laboratory. Such work is essential to the vigorous growth of the subject.

Mr. Dykes emphasised the importance of limit gauges in all classes of manufacture, even of such things as ploughshares and perambulator wheels. He recommended that the National Physical Laboratory should have two classes of tolerances for commercial gauges, the lower class being suitable for coarser work. He urged the more widespread use of the screw gauge protector.

Mr. M. F. Ryan (Director of Munition Gauges) said the early production of gauges was seriously hindered by the measurements on the standards from which the drawings were being made being inaccurate, so that gauges correctly made to the drawings might not fit the standards. When the National Physical Laboratory took over the testing this state of affairs was quickly exposed. The work of teaching the manufacturers was also carried out by the N.P.L., and it is largely due to this that the large output (10,000 per week before the armistice) was secured. He was heartily in favour of Dr. Shaw's suggestion of setting up a metrology department in the universities.

Mr. J. E. Sears (Supt. Metrology Dept., National Physical Laboratory) said the intimate association with manufacturers of gauges and also of the products for which the gauges were intended, had given them an opportunity during the war of attaining quite exceptional progress in the subject. He thought limit gauge work was going to be an important factor in all future engineering; and, if interchangeability between the work of different firms had to be maintained, it is evident that all the controls of such gauges must be referred to a central authority governing the fundamental standards of length. It was essential that the Laboratory should also have a fair amount of test work in order to maintain the close contact with the manufacturers that had proved so useful in the past. There would still, of course, be plenty of work for local centres, which he agreed were desirable; but he did not think the universities were the most suitable places for such work to be carried out.

Mr. W. H. Bolton (University of Sheffield) emphasised that education was necessary among manufacturers before they would realise that standardisation was essential to efficiency in their business. In Sheffield one firm made 1700 different patterns of pocket knife. He thought a scheme of decentralisation was vital to the nation, and he disagreed with Mr. Sears as regards the relation of the universities to test work. He regarded test work as essential if these institutions were to keep in touch with industrial requirements.

Mr. B. P. Dudding (of the National Physical Laboratory) said that in nearly every case when one comes to apply measuring to a specific problem one has to conduct some researches as to how the measurements should be made, what instrument to use, and how to use the instrument. The research worker needs to have a good workshop behind him.

Sir Richard Glazebrook, in replying to the discussion, expressed his satisfaction at the interest in the subject which was evidently springing up all over the country.

The President, in closing the meeting, said that several points of importance were brought out prominently throughout the discussion. These were first, that under the stress of the war many manufacturers have learned to use limit gauges with very great improvement to their work. Second, that there is a tendency to slip back into old methods, which must be vigorously resisted. Third, that sub-stations where accurate testing could be carried out locally, in close association with the National Physical Laboratory, were essential to the future development of metrology.

An exhibit of Optical Scales and Graticules, by Mr. J. Rheinberg, was on view at the close of the meeting.

Black Varnish for Wood can be made by dissolving bitumen in carbon bisulphide. If the odour is objected to, carbon tetrachloride can be used instead of bisulphide.

NOTICES OF BOOKS.

Applied Optics: The Computation of Optical Systems. Being the "Handbuch der Angewandten Optik" of Dr. Adolph Steinheil and Dr. Ernest Voit. Translated and Edited by James Weir French, B.Sc. Glasgow and Bombay: Blackie and Son, Ltd. Two Volumes. Price 12s. 6d. net each.

The present work, an edited translation from the Standard German work of Steinheil and Voit, is issued with the approval of the Standing Committee on Glass and Optical Instruments appointed by the Advisory Council of the Department of Scientific and Industrial Research, in order to provide the British Optical Industry with a handbook presenting a complete Trigonometrical System of Optical Computation in a form suitable for practical use.

Mr. James Weir French, B.Sc., of Messrs. Barr and Stroud, Ltd., who is himself a member of the above Committee, is responsible for this edition in English. Through his wide experience in optical productions he has been able to supply a work that is eminently suited to the practical conditions of the present day. It is thus not a mere translation; it owes much to Mr. French's own specialist knowledge of a highly technical subject.

A distinguishing and essential feature of the original work is the very complete system of symbols and sign convention employed. The portion of the original appendix which deals with this has been included in both volumes. To illustrate the meaning of the symbols there has been added a series of ten diagrams over and above those that appear in the original. These diagrams include examples descriptive of the sign convention.

The diagrams form an important element in the work. To render them abundantly clear they are printed in colours, whereby their convenience for ready reference is greatly increased.

NOTES.

Recently we had had occasion to turn up No. 1 of the Chemical News, published on Saturday, December 10, 1859. It was edited by William Crookes, and the general appearance is much the same as to day's issue. The matter is interesting. The first paper is by C. Grenville Williams on "Vapour Volume," and we read about oxygen with an atomic weight of 8, and are warned that it is safer to adhere to the old notation until further researches have shown its fallacy. The table of contents contains papers on the "Separation of Nickel and Cobalt from Peroxide of Iron" and on "Platinum and its Associated Metals," by MM. Deville and H. Debray. The metal had been introduced into the laboratory but a few years back, and speculations are raised as to its possible uses. The paper is chiefly occupied with the metallurgy of platinum and can be studied with profit to day. A paper by John Spiller, F.C.S., deals with the production of a carbon ink, in which concentrated sulphuric acid, indigo, sugar, and gum are used; the author mentions the need for using a gold or a quill pen, and also the fact that the paper must needs be thick as the written characters *penetrate* somewhat! In the "Proceedings of Societies" a meeting of the Chemical Society is reported, with B. C. Brodie, F.R.S., in the chair, and we read discussions in which Dr. Hofmann, C. L. Bloxam, Dr. Miller, and Dr. Odling take part. The advertisement pages, too, are interesting; many familiar names appear. James R. Gregory offers collections of minerals; Churchill, Van Voorst, Mitchell, and others offer books. "Elements of Chemistry," by William Allen Miller, is announced as just published. The principal difference between the first issue and that of to-day is the presence in the former of

matter and advertisements dealing with pharmaceutical chemistry and medicines. On reading through the issue it is impossible not to notice the tremendous advance in the chemistry of to-day over that of sixty years ago, an advance that we can confidently assume will continue; so that the subscriber to the CHEMICAL NEWS sixty years hence may find as much interest in reading to-day's issue as we do in reading Prof. Bloxam's demonstration at the Chemical Society of the decomposition of ammonia by means of the discharge from a Rühmkorff coil.

THE Second "Report on Colloid Chemistry" has just been published; the first report was issued in 1917 by the British Association for the Advancement of Science, but on account of financial difficulties consequent on the War they were unable to meet the greatly enhanced cost of publication for the Second Report. Under these circumstances, and in view of the importance of the subject, the Department of Scientific and Industrial Research has arranged that this Second Report should be published by H.M. Stationery Office, and it is now on sale at 1s 6d. net. The work occupies some 170 pages and is very complete: historical matter, practical applications, and theory are exhaustively treated, and the publication will be found of very great value in almost all industries.

AUTOMATIC AND ELECTRIC FURNACES, LTD., of 281-283, Gray's Inn Road, W.C. 1, have designed and placed on the market a series of electric muffle furnaces that are likely to become of use in chemical and technical laboratories. They appear to be of simple and robust construction; they are capable of giving temperatures up to 1000° C. and are wound for any voltage between 100 and 250 volts for continuous or alternating current circuits.

IN a paper on "Some Observations on the Use of Boric Acid as a Disinfectant," Fred W. Tanner and Ruth S. Funk (Bacteriological Laboratory, University of Illinois, Urbana, Ill.) give an account of some carefully conducted experiments showing the effect of this agent on a number of bacteria. A saturated solution of boric acid in distilled water was used and tubes of dextrose agar were inoculated and incubated. The result showed that very little if any germicidal action followed the use of even large amounts of boric acid. Further experiments were made using the silk thread method of inoculation, which also gave a very poor result, and the general conclusion of the authors is that the use of this reagent should be discontinued in those cases where disinfection is absolutely essential.

BERI BERI, a disease prevalent in Eastern Asia, has been found to be very common where polished rice was the main article of diet. On treating patients suffering from the disease with extracts from the husks and polishings removed from the rice marked improvements were noted. It appears that the "vitamines" contained in the husks of rice and other grains are very necessary, and their removal may lead to unhappy results.

SIR JOSEPH J. THOMSON, O.M., President of the Royal Society and Master of Trinity College, Cambridge, has been appointed by an Order of Council dated May 8, 1919, to be a member of the Advisory Council to the Committee of the Privy Council for Scientific and Industrial Research.

THE Institute of Chemistry is operating with the Appointments Department of the Ministry of Labour in view of the resettlement in civil life of chemists who have served with the forces. The Council is said to have stated that "Salaries of £300 a year and upwards (with prospects) would command a good selection of candidates." This statement has given rise to some comment on account of the smallness of the minimum suggested, but unfortunately we are in possession of information that shows that salaries of considerably less than this have been offered and accepted by chemists who, upon demobilisation, have found great difficulty in obtaining appointments.

PIEZO-ELECTRICITY, the production of electricity by pressure upon crystals, although observed many years ago, has only been applied to practical uses of late years. The matter was studied exhaustively by M. Curie, who devised and used an instrument based upon the principle in the early work upon radio-activity that led eventually to the discovery of radium. To M. Curie is due the discovery that the quantity of electricity developed in a crystal by pressure is exactly proportional to the pressure. Sir J. J. Thomson has recently drawn attention to the phenomena in a lecture delivered at the Royal Institution, and suggested the possibility of using it for the measurement of suddenly developed pressures such as are met with in artillery and explosion of gun-cotton, &c. Explosions have been recorded lasting only 1/100,000th sec. The method is likely to find many applications in the near future.

GRANTS FOR SCIENTIFIC RESEARCH IN SOUTH AFRICA—The Research Grant Board which has been established by the Union Government in South Africa for the encouragement of scientific research, has recently announced its scheme for awarding research scholarships and making grants towards the expenses of scientific research. The scholarships will vary in value from £80 to £250 per annum for one or two years, and may be awarded for a further period. Applications must be made through, and with the approval of, one of the governing bodies of the higher educational institutions of the Union or of a Museum or Research Institute. H.M. Senior Trade Commissioner in South Africa has forwarded the Regulations of the Board, and these may be consulted at the Enquiry Room of the Department of Overseas Trade.—*Board of Trade Journal.*

NOTES FROM FOREIGN SOURCES.

Graphitic Carbon and Graphitic Acid. — V Kohlschütter and P. Haenni.—By graphitic acid the authors mean the solid oxidation products which are obtained by subjecting pure graphite, prepared electrically, to the action of a mixture of nitric acid, sulphuric acid, and chlorate. It is essential that the oxidising mixture should be taken up by the whole mass of graphite, and that the chemical action should take place simultaneously from the interior. This is brought about by the nitric acid; oxidising agents which do not penetrate into the substance lead only to the simplest oxidation products. When the oxidising action is repeated the proportion of carbon in the product is gradually decreased, and the flakes of graphitic acid dissolve to form reversible colloid products. When dry graphitic acid is heated to 200° carbon separates, water, CO, and CO_2 being simultaneously formed. The carbon thus obtained possesses all the properties of soot, but it can comparatively easily be compressed to give a dense mass of a graphitic nature. Sulphuric acid also decomposes graphitic acid at 160—180°, giving CO and CO_2 in proportions which depend upon the way it is heated. Reducing liquids produce carbonaceous products resembling the original graphite, mixed with by-products of the reaction. The experimental results seem to show that there is no essential difference between amorphous carbon and graphite, and the peculiar properties of the latter are due to a peculiar state of division and dispersion.—*Zeitschrift fur Anorganische und Allgemeine Chemie*, 1919, cv., 121.

Cyclisation by Elimination of a Nitro Group.—S. Reich and V. Nicolaeva.—The authors have prepared the oxime of 2.4-dinitroacetophenone by the action of amyl nitrite upon 2.4-dinitroethylbenzene in presence of sodium

alcoholate. When the oxime is heated for a quarter of an hour with 15 per cent hydrochloric acid and water is added, the phenylhydrazone of 2.4-dinitroacetophenone is obtained, and this yields methyl-nitro-indoxazene on the addition of aqueous soda to its alcoholic solution in the cold. The cyclisation takes place with elimination of nitrous acid. Secondary products are also obtained by the reaction, but the authors have not yet studied them. The most abundant product is methyl-nitro-indoxazene, which can be purified by crystallisation in alcohol; it forms yellowish crystals which melt at 114°. -*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 190.

Action of Alcoholic Potash on Resins — Paul Nicolardot and Charles Coffiqsier.—The authors have studied the action of alcoholic potash on different resins, heating 1 grm. of the resin for an hour with 25 cc. of N/2 alcoholic potash, using a reflex condenser. 50 cc. of water were then added and the insoluble residue was filtered off and weighed. Of the twenty-seven different types of resins examined, all but one left an insoluble substance, and the addition of water enabled them to be classified in three groups:—(i.) Those with which the amount of insoluble product was unaffected by the addition of water; (ii.) those with which the addition of water led to the total or partial disappearance of the insoluble part; (iii.) those which showed an increase of the insoluble part when water was added. It appears that the action of alcoholic potash gives rise to resinous soaps, some of which are more soluble in alcoholic potash than in water, while others, on the contrary, are more soluble in water than in alcoholic potash. It is possible that this new characteristic may be employed in the identification of different resins.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 200.

Mobility of Hydrogen Atoms in Organic Molecules. Action of Phenyl Hydrazine on Dioxindols.—J. Martinet.—Among the factors which may influence the mobility of hydrogen atoms two are specially important—the neighbourhood of electro-negative elements and a particular position with regard to double bonds. If two atoms α and β are united by a single bond an atom of hydrogen attached to α is mobile if β has a double bond. In dioxindol one atom of hydrogen is thus placed, while another is united to an atom of oxygen. Hence, although the carbonyl group of the dioxindols has a lactamic and not ketonic character, the structure of these substances recalls that of the α ketonic alcohols, which with phenyl hydrazine give diphenyl hydrazones or osazonee. If the readiness of the secondary alcoholic function to undergo oxidation is due to its position with regard to the double bond of the ketonic group, a similar action on dioxindol might be foreseen, one molecule of phenyl hydrazine acting as oxidising agent, while a second entered into combination. Experiment has confirmed this hypothesis, which the authors have verified in the case of dioxindol and five of its homologues chosen from different groups. The reaction must be carried out in an atmosphere of hydrogen, and various media, such as water, alcohol, acetic acid, or mixtures of these three, were tried. In all cases the reactions were practically instantaneous at the boiling-point of the solvent and the yields were good.—*Comptes Rendus*, 1919, clxviii., 689.

Reaction of Aconitine.—L. P. J. Palet.—Dragendorff has stated that a characteristic reaction of aconitine is the formation of a reddish coloration when it is heated with phosphoric acid. Other observers have failed to obtain this coloration or have noticed it only with impure specimens, such as the aconitine obtained from the organs of animals poisoned by this alkaloid, which might be explained by supposing that it was due to the presence of a decomposition product. The author has obtained positive results with two samples of amorphous aconitine, using concentrated phosphoric acid and heating directly over a small flame until fumes were given off. A violet coloration was thus produced, while with crystallised specimens only a greyish colour was obtained, as Barthe has previously stated. If the reagent employed is a mixture of phosphoric acid and sodium molybdate, in the proportions of 25 to 1 by weight, a very intense violet coloration is obtained even with crystallised specimens which were unaffected by phosphoric acid alone. Many other products, such as apomorphine, atropine, brucine, cocaine, &c., were tested similarly, and although they gave various colorations the only ones which could be confused with those obtained with aconitine were aspidospermine and veratrine. These, however, can readily be distinguished from aconitine by trying the effect of oxidising agents on the first and on mineral acids upon the second.—*Journal de Pharmacie et de Chimie*, 1919, xix., 295.

Action of Phenyl Magnesium Bromide upon the Polyhalogen Derivatives of Ethane. Fred Swarts.—The author endeavoured to obtain fluorstyrolene by the action of phenyl magnesium bromide upon difluordibromethane, expecting to get difluorbrom methyl benzene which, with alcoholic potash, would yield difluorstyrolene. But the products actually obtained were difluorethylene and brombenzene. Thus the magnesium compound acted as a reducing agent, *removing two atoms* of bromine. Various polyhalogen derivatives of ethane were then submitted to the action of phenyl magnesium bromide, and it was found that the principal reaction with bromine derivatives was the subtraction of two atoms of halogen, with the production of brombenzene and an ethylenic derivative. When an atom of carbon was united with fluorine and bromine the latter was removed. With chlorine derivatives a molecule of hydracid was removed, and this reacted with the magnesium compound to give benzene. In many cases magnesium fluoride was obtained, but was present in a colloidal state. Various secondary reactions also took place, diphenyl being frequently formed, especially in the case of reactions which take place slowly.

MEETINGS FOR THE WEEK.

Monday, June 2.

Royal Institution, 5. (General Meeting).
Royal Geographical, 5.30. (Anniversary Meeting).

Tuesday, June 3.

Royal Institution, 3. "Listening under Water," by Prof. W. H. Bragg.
Institution of Electrical Engineers, 6. "Continuous Wave Plant at the Carnarvon Station," by Senatore G. Marconi.
Röntgen Society, 8.15. (Annual Meeting).

Wednesday, June 4.

Society of Public Analysts, 8. "Examination of Commercial Samples of Nicotine," by Percival J. Fryer. "Mexican Insects in Poultry Food (Notonecta, Corixa, and Mexican Cantharides)," by T. E. Wallis. "A Rapid Method for Determining Nickel and Cobalt in Ores and Alloys.—Part. III.," by W. R. Schoeller and A. R. Powell. "Notes on the Oil of Ceratotheca sesamoides," by E. Richards Bolton. "An Improved Method for the Estimation of Nitrates in Water by means of the Phenolsulphonic Acid Reaction," by Robert C. Frederick. "Estimation of Morphine in Indian Opium," by Jitendra Nath Rakshit and Frank J. D'Costa.

Thursday, June 5.

Royal Institution, 3. "The Balkans," by Sir Valentine Chirol.
Royal Society of Arts, 5.30. "Aviation as Affecting India," by Brigadier-General Lord Montagu of Beaulieu.

Friday, June 6.

Royal Institution, 5.30. "Atomic Projectiles and their Collisions with Light Atoms," by Prof. Sir Ernest Rutherford.

Saturday, June 7.

Royal Institution, 3. "The Italian Front," by J. M. Price.

THE CHEMICAL NEWS

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THEORY OF ALLOTROPY: ALLOTROPES AND ALLOTROPOIDS.

By MAURICE COPISAROW.

THE term *allotropy* was first introduced by Berzelius (*Jahresb.*, 1841, xx., 11, 13) as denoting the appearance in several states, distinguished from each other by different properties, a definition lacking in precision, owing to the numerous possible interpretations of the "different properties." This vagueness is put forward as a guiding principle by Lothar Meyer (Watts' "Dictionary of Chemistry," 1888, i., 128), who considers that the notion of allotropy is not to be defined with perfect exactness.

Allotropy is taken as a term covering the different physical states of matter, and also isomerism, polymerism, and polymorphism (Lehmann, "Zeit. Krystal. Min.," 1877, i., 97; Lowry, *Trans. Faraday Soc.*, 1916, ii., 150), and in this sense might appear, perhaps, to be an unnecessary term without exact meaning in chemical nomenclature.

This inclusion of different phenomena, along with Ostwald's and Nernst's definition of allotropy on the basis of energy changes, and Benedick's, Honda's, and Le Chatelier's conception based upon the discontinuity of forms, phases, and properties, is due to the consideration of *effects of* instead of *causes* underlying phenomena.

Whilst the close study of various properties of matter consequent to a certain phenomenon may help us in comprehending the phenomenon itself and its relation to other natural manifestations, it is wrong *to define* a phenomenon by its effects, especially when these effects are anything but specific or characteristic.

A far truer and more productive definition would be based upon the study of the causes of a phenomenon, the unmasking of which should naturally throw much light upon the phenomenon itself and its probable effects.

The possible causes of allotropy may be either—(1) a variation in the intra-molecular structure of elements; or (2) a change in the inter-molecular association or aggregation of elements.

Considering that—

I. Molecular aggregation subject to the laws of crystallography accounts for polymorphism (Wyroubow, *Bull Soc. Min.*, 1906, xxvi., 335), and that

II. Allotropic modifications present in most cases considerable chemical and physical differences—it would appear that allotropy is due to intramolecular differences (Koppel, *Naturw. Rund.*, 1904, xix., 249, 261; Guthrie, *Journ. Roy. Soc. N.S. Wales*, 1911, xlv., 318; Oxley, *Trans. Faraday Soc.*, 1916, xi., 129).

We can not only regard allotropy as a function of valency, but also define it as the capacity of an element to exist in forms, differing in the mode of their intra-molecular linkage.

This conception is in full accord with the (1) hypothesis of dynamic allotropy (Smits, *Proc. K. Akad. Wetens. Amsterdam*, 1910 and onward), as on this basis only a simple space lattice, revealed by the reflection of X-rays from the internal planes of crystals, can be deduced, and (2) the *view* of different ions existing in solution in presence of two allotropes of an element (Holt, *Journ. Soc. Chem. Ind.*, 1915, 693).

In this sense allotropy, although a function of valency, does not imply isomerism or polymerism, as all allotropes need not necessarily contain the same or a multiple number of atoms in their respective molecules.

The conception of allotropy as a function of valency can be clearly understood on the basis of the electronic theory of the latter.

According to this theory the valency bonds are considered as having a definite direction. The relative direction of these bonds in the molecule may be influenced by the conditions under which such a molecule is formed. Variation in the direction would give rise to molecular structures differing in the distribution of the electric charges among the constituent atoms. These would be allotropes, and that configuration in which the charges were most symmetrically arranged or neutralised would be the stable form under these conditions (Holt, *loc. cit.*)

(This conception is closely related, if not identical, with the atomistic hypothesis according to which allotropy is due to changes in the electric and magnetic charges of an atom (Dumas, *Ann. Chim. Phys.*, 1831, [2], xlvii., 324; Howe, *Rep. Brit. Assoc.*, Sheffield, 1910 p. 562), as intramolecular structures are primarily due to the properties and functions of the atoms).

Recognising allotropy as a function of valency and knowing the valency of an element (maximum in case of elements of variable valency), we should be able to indicate *not only the possible constitutional formulæ of* allotropes, but also the maximum possible number of allotropes for each individual element. (Without necessarily defining the number of atoms in the molecule, although the constitutional formulæ may in turn throw occasionally much light upon the complexity of the allotropes).

Attempting to represent elements by structural formulæ on the basis of their valencies, we find that monovalent elements can exist in one and only one molecular form (disregarding the ionic or nascent state), divalent elements may have two distinct allotropic forms. (Should elements exist in monoatomic molecules the number of modifications will be augmented by one):—

(*a*) A molecular structure in which both valencies of the atoms are fixed, and

(*b*) A molecular structure in which some valencies are free.

In the case of trivalent elements two allotropes are possible, being—

(*a*) A saturated molecular configuration, in which all valencies are fixed, and

(*b*) An unsaturated molecular configuration, in which some valencies are free.

In case of tetra-, penta-, and other polyvalent elements three allotropic forms are possible, being—

(*a*) A rigid molecular form, in which all valencies are fixed;

(*b*) A rigid molecular form, in which some valencies are free; and

(*c*) A non-rigid molecular form, in which some valencies are free.

(On the basis of symmetry it is unlikely that a semi-rigid configuration, in which some atoms are rigidly fixed, whilst others retain the power of free rotation, should occur).

By molecular rigidity the author implies rigidity of atoms constituting the molecule, a rigidity caused by the fixation of the valencies. It appears that whilst an atom linked to two other atoms has the power of free rotation (the valencies being regarded as an axis), an atom linked to three or more atoms has no such power of rotation and can be regarded as rigidly fixed.

This gives the maximum number of distinct allotropes of an element under the most favourable conditions of temperature and pressure, forms possibly but not necessarily occurring in all physical states.

The examination of the chemical and physical properties of any element should enable us to determine the intra-molecular structure of each allotrope.

In trying to develop this hypothesis we must avoid a fallacy so general to many theories; *i.e.*, being one-sided

in regarding various phenomena either as identical or totally disconnected with one another.

Continuity, harmonious continuity, is the most striking feature of natural phenomena when viewed as a whole.

The examination of separate most advanced members of any group, series, or species shows discontinuity, but continuity becomes manifest as soon as an effort is made to survey any phenomenon in all its gradations.

This certainly applies to such manifestations as physical states of matter, polymorphism and allotropy. The physical states of matter in their crystalline form, solid and liquid crystals, connect physical states with polymorphism. Polymorphism is, on the other hand, closely connected in many instances with allotropy.

A scrutiny of the possible molecular forms of elements shows that theoretically it is possible for an element to have in certain cases more than one molecular form corresponding to each mode of linkage indicated above; that is, there may occur more than one form of an element with a *non-rigid* or *rigid* configuration. But regarding allotropes as the most chemically and physically distinct forms of an element it is obvious that several molecular forms containing a different number of atoms, but all having the power of free rotation, will differ among themselves to a less extent than when compared with a molecular structure of the same element, in which all atoms are rigidly fixed.

Thus it follows that valency and the saturation or fixation of the atoms, and not the actual number of atoms, play the predominant part in the determination of allotropes. In this light allotropy becomes the capacity of an element to exist in forms differing in the mode of their intra-molecular linkage.

Molecular forms differing in the number of atoms or distribution of linkages, but all belonging to one and the same type of mode of linkage indicated above, can be termed *allotropoids*. These molecular forms serving as teh transition or link between polymorphism and allotropy proper can be compared with the cryptoisomeric substances (Pfeiffer, *Ber.*, 1916, xlix., 2426; 1918, li., 554).

Each modification of an element, which is an *allotropoid* in relation to forms belonging to the same mode of linkage is an allotrope, when viewed in connection with modifications belonging to a different type of linkage.

Allotropoids will differ among themselves less in physical and still less in chemical properties than *allotropes* of the same element.

The problem of discriminating between allotropy and polymorphism, or intra- and inter-molecular structures, comparatively easily solvable in the case of a few advanced characteristic instances, becomes therefore complicated and the available methods uncertain, not only owing to the inert character of some elements, which compels us to draw conclusions from their physical properties only, but also owing to the fact that in some cases we may deal with substances which are simultaneously either—(1) allotropes and polymorphic forms, or (2) allotropoids and polymorphic forms.

Thus the physical data may indicate the combined effect of intra- and inter-molecular rearrangements in the element, and as the components, the combination of which gives us the total effect, need not necessarily be magnitudes in the same direction, the physical data lose much even of their comparative value.

The knowledge of the maximum possible number of allotropes, serving as a guiding limitation, augmented by the chemical and physical properties of the modifications should be sufficient in most cases in identifying the allotropes of an element. In cases where owing to the inertness of an element we have to depend upon the physical factor only, as many physical properties as possible are to be taken into consideration, as no single feature or property is sufficiently characteristic as to serve as a decisive indication of allotropy.

The functional connection of physical constants with the periodic system of atomic weights and volume of elements make it very necessary, if any generalisations are to be made, to have the experimental conditions for the determination of physical constants specific for every element with special relation to the absolute melting and transition points of every modification of an element.

Differences in crystalline symmetry are indefinite as a criterion or definition of allotropy owing to the possibility of substances belonging either to different crystalline systems or different classes of the same system. The observation that the higher the crystalline symmetry of an element the smaller is the number of atoms constituting its molecule (Relgers, *Zeit. Phys. Chem.*, 1894, xiv., 1), and consequently the smaller is its tendency to allotropy (Barlow and Pope, *Journ. Chem. Soc.*, 1906, lxxxix., 1741) is of an empirical character, and can hardly serve as a guiding principle in distinguishing between allotropic from polymorphic forms, this being specially so as crystalline structures may depend at least as much upon molecular aggregation as on the intra-molecular configuration of the atoms.

The sudden changes in and the discontinuity of properties can be accepted as an indication of allotropy, but with reserve, not only owing to the difficulty of establishing such discontinuity (Honda, *Journ. Iron and Steel Inst.*, 1915, ; *Science Rep.*, Tokio, 1915, [IV.], No. 3, 261), but also owing to the fact that such changes accompany both allotropy and polymorphism, and if there is any difference it is in the degree not the kind of change.

The thermal changes so characteristic of the most pronounced allotropic transformations of the non-metallic elements, though often very useful as an indication, are not completely to be relied upon, as all thermal measurements for metals give decidedly lower values than for non-metals, and considerable changes of volume, hardness, porosity, electromotive forces, electrical resistance, specific heat, and thermoelectric power are not necessarily accompanied by great heat changes.

Considerable heat changes may be taken as a positive indication of allotropic rearrangement, but small heat changes are hardly safe as a negative proof, the more so as the heat evolution actually recorded may be the sum of two or more values or reactions, some exothermic and others endothermic.

As mentioned above, the allotropes of metals are more difficult to isolate and distinguish than those of the non-metals owing to their inert character. But even in cases where no separate allotropic modifications were isolated, (1) the dependence of such physical properties as density, specific heat, expansion, electrical conductivity, and the melting, solidification, and transition points upon the thermal history of the specimen, and (2) the variation of the chemical behaviour with the past history of the metal—are best explained on the basis of the allotropy hypothesis.

The occlusion of hydrogen by palladium and palladium black, the etching of iron by nitric acid, and the solubility of carbon in α and γ iron can be quoted as such extreme cases.

The *constitutional formulæ* of allotropes developed on the basis of valency and the chemical and physical properties of each modification, although not actually solving the interesting problem of molecular complexity, offer us substantial aid in this respect, in so far as they often indicate the minimum molecular complexity satisfying the requirements of the formulæ.

His Majesty the King, on the recommendation of the President of the Board of Trade, has been pleased to award the Silver Medal for Gallantry in Saving Life at Sea to each member of the crew of the Danish s.s. *Mary*, which rescued Mr. Harry George Hawker and Commander Kenneth F. Mackenzie-Grieve, R.N., in the North Atlantic on May 19. The Board of Trade, with approval of His Majesty, have also awarded pieces of plate to the master of the ship and to the person in charge of the rescuing boat, and sums of money to the rest of the boat's crew.

A PRECISION PRESSURE GAUGE.*

By EDWARD J. BRADY.

THIS note is a brief description of a precision pressure gauge of high sensibility and great accuracy recently constructed at this Laboratory.

In principle it is virtually a large diameter U-tube (6 cm. diam.) filled with some transparent non-volatile, non-oxidising liquid such as kerosene or paraffin oil. In each leg is placed a hollow brass float. The two floats are connected together with a fine silk thread which passes downwards around a light graduated wheel with jewel bearings immersed in oil at the bottom. The position of the wheel, which is provided with a vernier, is read through a glass window in one end of the box that forms the bottom of the gauge.

Laboratory workers having to do with the accurate measurement of small gas pressure, either plus or minus, are greatly in need of an instrument similar to the one to be described.

The way in which the differential pressure enters in the formulæ for both the Venturi meter and the Pitot tube may be represented by $P = (f)\ Q^2$, where P is the pressure that must be read and Q is the quantity of material passed. It will be seen that both of the methods become increasingly inaccurate at low velocity, because of the difficulty of measuring small pressures accurately. This gauge ought to increase the usefulness of both the Venturi and the Pitot tube.

A modification of the gauge with an opening to receive the horizontal velocity pressure of the wind might be used as an anemometer.

The two glass cylinders are cemented into the removable cover of a brass box, one end of which has a glass window. To the lower side of the cover is fastened the little yoke supporting the two jewel bearings in which the index wheel or drum revolves. To one arm of this yoke is fastened a projecting piece carrying a vernier flush with graduate surface of the wheel. There is a small groove on the face of the wheel around which passes the silk thread that holds the two hollow floats almost totally immersed in the fluid. Any pressure P on this liquid in one tube produces a linear motion at the circumference of the wheel of $\frac{P}{2}$

The diameter of the wheel was so chosen that a pressure of one inch of distilled water exerted on a paraffin oil, such as kerosene, produces a motion of the periphery of the wheel of 10 divisions. By the aid of the vernier this precision can be increased.

These cylinders are made of glass, so that the gauge can be read approximately and from a distance like an ordinary U-gauge with the inch mark on the scale between the two cylinders.

Its use as a zero reading instrument capable of indicating pressure differences of less than 10^{-3} inches of water, will now be described.

Upon the little shaft that carries the graduated wheel there is fastened a small mirror, arranged to face toward the glass window in the lower position. About 4 feet in front of the gauge there is mounted a telescope and scale. This can only be used for comparatively small variations in pressure, say less than 2/10''. However, the telescope and scale may be used to measure small differences at pressures of, say, 2''-3'' and 4'', by moving the mirror around on the shaft, so that it has the proper aspect when the gauge is subjected to the above pressures.

This is facilitated by a small bent movable wire, projecting through a stuffing box in the side. It is pushed in sufficiently to interfere with the rotation of the mirror until the float assumes the position corresponding with the pressure whose small variation is to be measured. It is then withdrawn, when the telescope and scale can be used as before.

The glass window may be made a section of a cylinder, so that all rays from the scale would pass normally through the glass, eliminating refraction effects, but this was not found necessary in practice.

The instrument as constructed has twin hollow brass floats and a brass wheel below. The bearings are jewelled, with very little friction. The friction may easily be made as near zero as is possible by making the wheel of aluminium and so proportioning it that the weight of the wheel *in the oil used* is just equal to the buoyancy of the two floats.

Even with the brass wheel having some weight on the bearings, the system has a very definite zero. The motion of the mirror for small displacements is almost critically damped.

The instrument may be dismantled by inserting two small wire hooks through the hose connections at the top to support the floats while the oil flows out at the bottom.

A gauge constructed as above described has been in use at this laboratory and has given entire satisfaction. When not in use a small piece of rubber tubing is connected from one inlet to the other to keep the dust out. With an ordinary U-gauge an accumulation of dirt invariably appears at the point where the menisci are read; with this gauge, however, the graduations on both the wheel and the vernier are immersed in the oil and always appear bright and clean.—*Journal of the Franklin Institute*, clxxxvii., No. 4.

* Note from the Physical Laboratory of the United Gas Improvement Company, U.S.A.

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS.*

By L. M. DENNIS and B. J. LEMON.

Historical.

BUT little attention appears to have been paid to the possibility of separating the rare earths by electrolysis of aqueous solutions of their salts. Edgar F. Smith (*Ber.*, 1880, xiii., 751) stated that "didymium is not precipitated, either as nitrate or acetate, although a partial precipitation takes place at the positive pole." Brauner (*Monatsh.*, 1882, iii., 1) electrolysed a solution of didymium acetate using platinum electrodes. There formed on the negative pole a pale red crystalline crust which contained didymium and acetic acid. Solutions of the nitrate and of the sulphate of didymium gave similar products. Brauner's object in these experiments was to ascertain whether a superoxide would appear on the positive pole. No such formation was noted, and he did not pursue the subject further. In a brief article entitled "Electrolysis of Solutions of the Rare Earths" (*Zeit. Anorg. Chem.*, 1893, iii., 60) Krüss makes the following statement:—"A solution of a chloride of a rare earth behaves upon electrolysis like a solution of an hydroxide in dilute hydrochloric acid; chlorine and hydrogen are set free at the electrodes, the solution loses more and more hydrochloric acid, and as the amount of the solvent diminishes, the hydroxide of the earth is precipitated in increasing amount. In this manner the rare earths can be removed from chloride solutions of mixtures of the earths, the amount thus precipitated depending upon the strength of the current and the duration of the electrolysis. It is to be expected that those bases which are the weakest toward hydrochloric acid will first be precipitated as hydroxides as soon as a part of the hydrochloric acid is decomposed by the electrolysis. The stronger bases will remain in solution as the more stable chlorides. In order to remove the hydrochloric acid uniformly from all parts of the solution

* From the *Journal of the American Chemical Society*, xxxvii, No. 1.

of the chlorides of the rare earths, electrodes of large surface were employed." Krüss electrolysed the solution for ten minutes, and then removed the heavy, dense deposit of hydroxide by filtration. The solution was then again electrolysed for ten minutes, and in this manner small fractions of less than 1 grm. each were obtained. Two electrolyses of solutions of impure yttria were carried out, and determinations of the atomic weights of the earths in the several fractions showed that the method gave quite rapid separation of the different earths. Krüss states at the close of this brief article that electrolysis of solutions of the rare earths might prove suitable for the separation of these elements. It does not appear, however, that he followed the matter further.

Considerable work has been done upon the anodic oxidation of cerium through electrolysis of solutions of cerium salts with platinum electrodes, but inasmuch as this does not concern the direct separation of the earth from solution upon electrolysis, the researches upon this subject will not here be reviewed.

Experimental.

Material.—The material that was employed in the experiments described below consisted of the earths of both the didymium and yttrium groups from which cerium and thorium had been removed. The earths of the didymium group were extracted from the crude double sulphates of potassium and the didymium group, a large amount of this material having kindly been presented to the writers by Dr. H. S. Miner, of the Welsbach Light Company. The lanthanum and praseodymium nitrates were prepared from quite pure samples of these two salts

Original solution.
Fract. 5.
Fract. 8.
Residual solution.

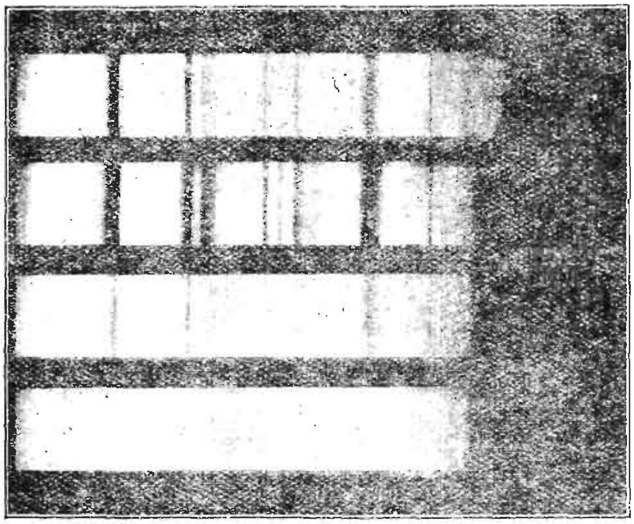
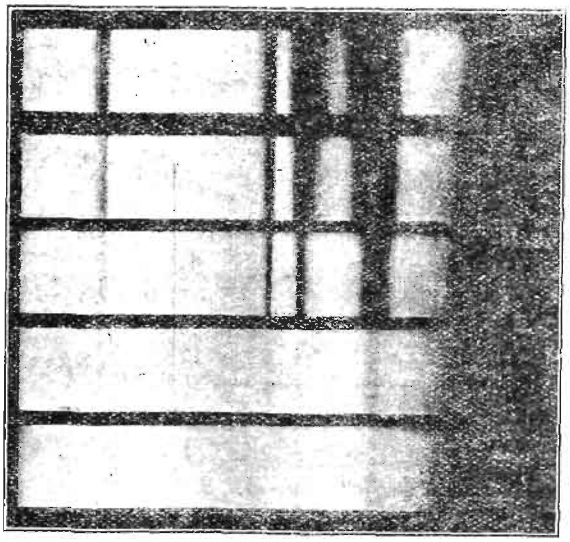


FIG. 1.

Original solution.
Fract. 4.
Fract. 5.
Fract. 6.
Residual solution



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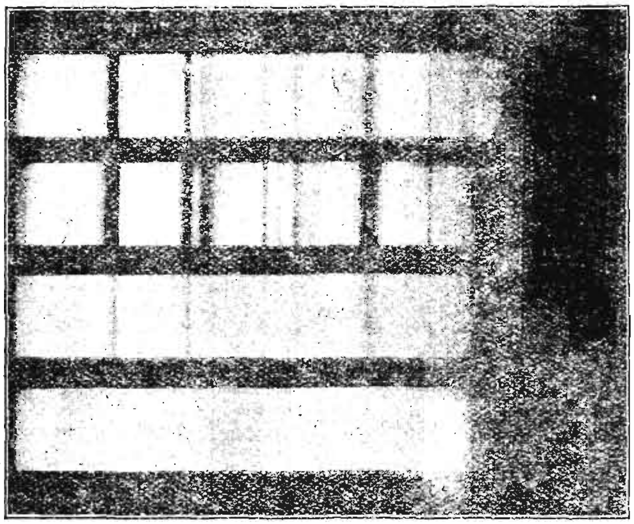

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Fract. 5.
Fract. 6.
Residual solution

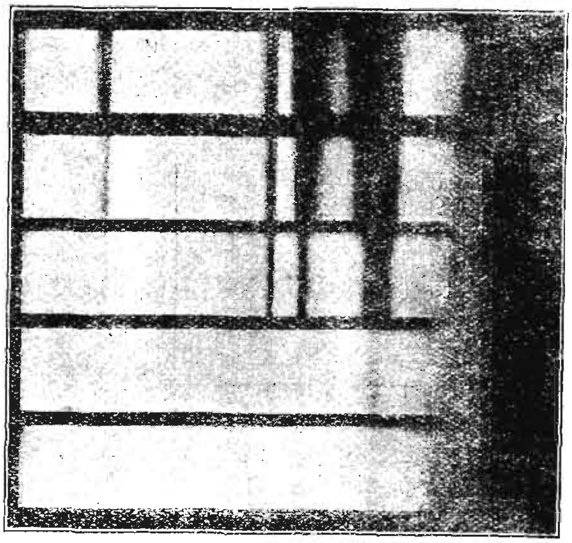


Fig. 2.

that we owe also to the kindness of Dr. Miner. The earths of the yttrium group were obtained from the crude rare earth oxalates from xenotime; the mixture that was used in the experiments showed strong absorption bands of erbium, and rather faint bands of europium, samarium, and holmium. The didymium bands were very faint.

Apparatus.—The first electrolysis was performed in a small crystallising dish and stationary electrodes of sheet platinum were used. On electrolysing a slightly acid solution of the nitrates of the didymium group, no precipitation appeared until the free nitric acid had been broken down by the current. As soon as this had been effected, however, a separation of the hydroxides of the earths appeared at the cathode, and the internal resistance of the cell rapidly increased. Upon interrupting the current and examining the contents of the cell it was found that a portion of the hydroxides had separated in flocculent form resembling aluminium hydroxide, and also that that part of the cathode which was immersed in the solution was heavily covered with a dense granular precipitate of the hydroxides. It was this coating of the cathode surface that interfered with the passage of the current and caused marked fluctuations in the voltage.

It was thus evident that no definite voltage could be maintained for any considerable length of time unless the cathode surface could be kept free from deposit of the hydroxides. To attain this end, a rotating cathode of copper in the form of a wheel 15 cm. in diameter and 2·5 cm. in thickness was next employed. This was mounted on a horizontal shaft of the same material and was set in such a position that the wheel dipped into the solution of the nitrates of the earth to a depth of three centimetres. An anode of platinum was used. A copper scraper was fastened in such position that it rested against the edge of the cathode wheel, and it was hoped that by means of this arrangement the deposit of hydroxides upon the cathode might rapidly be removed, and the voltage in this manner be kept sufficiently constant to permit of fractional decomposition of the different nitrates in solution. The apparatus did not give satisfactory results, and after thorough trial it was abandoned, and a mercury cathode was employed. The mercury was placed in a glass cell about 12 cm. in diameter and 13 cm. high, the layer of mercury being about three centimetres deep. The surface of this mercury cathode was kept clean by violently agitating it by jets of air, the air being conducted into the mercury through a glass tube with three outlets. The anode consisted of a piece of platinum wire 0·76 mm. in diameter. The source of current was a set of eight storage cells, an ammeter and variable resistance were placed in series with the cells and a voltmeter was connected in shunt with the cell. The aqueous solution of the rare earths that was to be subjected to electrolysis was placed in the cell upon the surface of the mercury.

I. *Separation of Lanthanum from the Other Earths of the Didymium Group.*

A neutral solution of the nitrates of the rare earths neodymium, praseodymium, lanthanum, and samarium, that contained 50 grms. of the oxides of the earth in one litre of the solution, was placed upon the mercury cathode in the cell, the mercury was set in agitation by a blast of air, the current was turned on, and the voltage was gradually stepped up to a point where fairly rapid precipitation of the hydroxides took place. The voltage was maintained constant at this value, 9 volts, throughout the series of fractionations, and this voltage was used in the three fractional electrolyses described below. The first fractional electrolysis was of six hours' duration. The current was then turned off, the hydroxides were allowed to settle, the clear supernatant liquid was siphoned off, and the remaining solution was separated from the precipitate by filtration through a Büchner funnel. The filtration was then returned to the cell and was again electrolysed. In this manner eleven fractions were obtained. The hydroxides of each fraction were first thoroughly washed with hot water, were then dissolved in hydrochloric acid, and the small amount of mercury that they were found to contain was removed by double treatment with hydrogen sulphide. The rare earths in the solution were then precipitated from a slightly acid solution with oxalic acid, were thoroughly wasehd, and were then ignited to the oxides. The atomic weights of the rare earth elements were determined by igniting one portion of the oxalate to oxide and determining the oxalic acid in another portion by titration with potassium permanganate. The details of this run are shown in Table I.

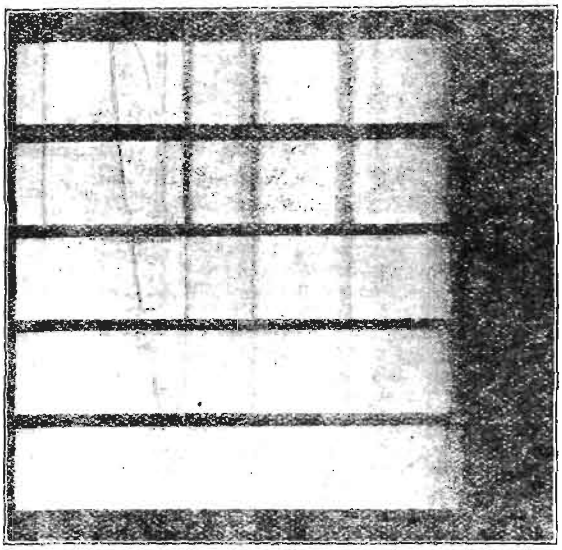
Original solution.

Fract. 3.

Fract. 4.

Fract. 5.

Residual solution.



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Residual solution.

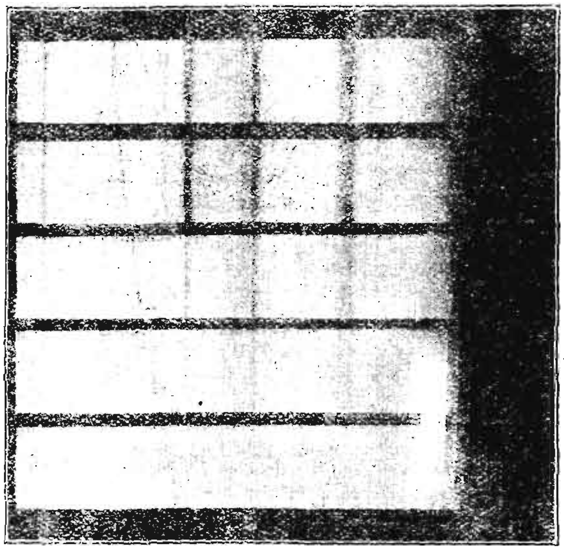

FIG. 3.

TABLE I.

Number of fractions.	Time in hours.	Colour of oxides.	Atomic weights (original material, 140·6).
1.	6	Light brown	140·9
2.	5	Light brown	141·2
3.	7	Light brown	141·5
4.	6	Light brown	141·9
5.	4	Colour fading	141·7
6.	5	Colour fading	141·0
7.	4	Colour fading	140·4
8.	5	Colour faint	139 6
9.	3	Colour very faint	139·5
10.	4	White	139·0
Residual solution		White	138·9

The absorption spectra of the original solution of Fractions 5 and 8 and of the residual solution were photographed with the aid of a Hilger wave-length spectrometer, Model 1912, with an oxyhydrogen zirconia lamp as the source of illumination. The different solutions used were of the same concentration in respect to the weight of the rare earth oxides contained in a unit volume. For photographs in black and white the Cramer trichromatic plate, which is especially sensitive to the red, was found to give quite satisfactory results. (Fig. 1).

II. *Separation of Lanthanum from Praseodymium.*

Nineteen and six-tenths grms. of fairly pure praseodymium dioxide and 18·9 grms. of lanthanum oxide were mixed, dissolved in nitric acid, the solution twice evaporated to dryness, redissolved in water, and diluted to 500 cc. Upon electrolysis of this solution the results showed in Table II. were obtained.

The atomic weights of the rare earth elements in these fractions were determined by the method mentioned under I. Inasmuch as praseodymium was present, the active oxygen in the ignited oxide was determined by the Bunsen method, and this was deducted from the weight of the oxide in order to arrive at the amount of Pr_2O_3 that was present. That the atomic weights of the earths in Fractions 1 to 4 inclusive were higher than that of praseodymium is due to the fact that small amounts of other earths of this group were present.

TABLE II.

Number of fraction.	Time in hours.	Colour of oxides.	Atomic weights (original material, 141·2).
1.	9	Black	142·1
2.	7	Black	141·9
3.	8	Dark brown	142·0
4.	9	Brown colour fading	141·7
5.	8	Brown colour faint	140·3
6.	7	Brown colour very faint	139·5
Residual solution		White	138·8

Photographs of the original solution, of Fractions 4, 5, and 6, and of the residual solution are produced in Fig. 2. It will be noted that lanthanum is freed from praseodymium by a very small number of fractional electrolyses.

III. *Fractional Electrolysis of the Earths from Xenotime. Separation of Erbium from Yttrium.*

Six fractional electrolyses were made with the results as set forth in Table III.

TABLE III.

Number of fraction.	Time in hours.	Colour of oxides.	Atomic weights (original material, 103·83).
1.	10	Light yellow	104.89
2.	8	Light yellow	111·00
3.	9	Light yellow	109·23
4.	7	Light yellow	99·73
5.	8	Faint yellow	93·50
Residual solution		Very faint yellow	92·08

Photographs of the original solution, of Fractions 3, 4, and 5, and of the residual solution are reproduced in Fig. 3. It will be noted that erbium concentrated chiefly in the first three fractions and that in the succeeding fractions its amount rapidly decreased. The atomic weight of the rare earths in the final fraction, No. 6, was 92, which demonstrates the rapidity of the concentration of yttrium by this method.

The results of the experiments here described upon the fractional electrolysis of different mixtures of the rare earths appear to warrant the statement that the method yields quite rapid separations of some of the rare earths, and that these separations can be effected with far less expenditure of time and labour than by the customary methods of fractional crystallisation or fractional precipitation.

MECHANICAL PHILOSOPHY AND SURFACE TENSION.

By FRED G. EDWARDS.

When an ether atom of mass $0·8 \times 10^{-24}$ grm. impinges upon a chemical atom of much larger mass the velocity of the ether atom is reduced in the proportion $f\mathrm{M}/(\mathrm{M}+m)$. Above the critical temperature and below the critical pressure of a gas, this would be compensated in the inverse ratio by the impact of a chemical atom upon an ether atom, so that the ether atoms in the interspaces of the gas would have the same average velocity as in the free ether. But, immediately the temperature is reduced and the pressure increased, the chemical atoms impinge upon each other to form the infinite molecule of the liquid or solid condition and the compensation of the ether atom is lost. This period corresponds with the formation of the meniscus in the vacuum tube or the tension surface surrounding the liquid. The reduction of ethereal atomic velocity produces a reduction of intrinsic pressure in the proportion $f_1[\mathrm{M}/(\mathrm{M}+m)]^2$, or a fraction of the ethereal pressure $0·5 \times 10^{24}$ dynes, of higher order than that of the critical or atmospheric pressure $\mathrm{N} \times 10^6$ dynes. The magnitude of the term $a/v^2 = 11,000$ atmospheres obtained from Van der Waals's equation $(p+a/v^2)(v-b) = \mathrm{RT}$, which is the estimated intrinsic molecular pressure of water, need no longer be surprising, as the intrinsic ethereal pressure is infinitely greater. Laplace's equation $\mathrm{P} = \mathrm{K} \pm \mathrm{H}/\mathrm{R}$ now admits of two opposing physical interpretations each a function of the mass and concentration of the molecules, one being direct action at a distance with an *assumed* radius of molecular attraction, and the other the measurable action of an incompressible fluid. In the latter case the intrinsic pressure is seen to be in reciprocal ratio to the compressibility, which is the elasticity of the material. It has been tacitly assumed that the free ether, and likewise the bound ether, are incompressible fluids; that is to say, the ethereal atomic volume is constant by reason of interaction through the tension surfaces.

The neutralisation of one monobasic acid molecule or of one ion of a polybasic acid at standard temperature yields $13,700/(6·1 \times 10^{23})$ calories with one electron. The heat of reaction is independent of the nature of the anion and cation, and equal to the quantity of heat required for the dissociation of water, which of course varies inversely with the temperature and therefore directly with the surface tension. The work required to force an electron into a metal or out of a liquid is thus a function of the surface tension, and likewise contact potential will be a function of the two surface tensions.

The difference in thermal energy of an electron inside a liquid and that of a free electron may be measured by the relative energies of its positive ether atom. The energy of the positive atom of free ether = 1·058 erg. can be calculated from two different data stated in grms. and centimetres :—

$$\mathrm{U} = \tfrac{3}{2}pv = \tfrac{3}{2}(5175 \times 10^{17})(1·39 \times 10^{-24}) \quad . \quad (1).$$
$$\mathrm{U} = \tfrac{1}{2}m\mathrm{C}^2 = 0·4\,\mathrm{C}^2 \times 10^{-24} \quad . \quad . \quad . \quad . \quad (2).$$

Incidentally from (1) and (2) the velocity of the ether atom is obtained. $C = 5{\cdot}193 \times 10^{10}$, or $3\sqrt{3} \times 10^{10}$ cms./secs. *This is* $\sqrt{3}$ *times the radiation velocity and* $\sqrt{3}$ is tan 60°, proving that the path of the ethereal atom coincides with four edges of a regular tetrahedron, thus completing the theory of an atomic ether described in a former paper (Chemical News, 1919, xcviii., 183), and showing that the atom does not reciprocate in a rectilinear path which would be the hypothetical alternative motion in a dodecahedral formation with double plena.

In the liquid the reduction of energy: –

$$\Delta U = 13{,}700 \times 4{\cdot}188 \times 10^{7}/(6{\cdot}1 \times 10^{23}) = 9405 \times 10^{-15} \text{ergs} \quad (3).$$

$$v = \text{constant} = 1{\cdot}39 \times 10^{-24} \text{ cc.}$$

$$\Delta p = \tfrac{2}{3}\Delta U/v = (6270{\cdot}3 \times 10^{-15})/(1{\cdot}39 \times 10^{-24})$$
$$= 4{\cdot}51119 \times 10^{11} \text{ dynes/cms.}^2 \quad . \quad . \quad . \quad . \quad (4).$$

In a dilute solution this would be the intrinsic molecular pressure of water. Hitherto it has been deemed impossible to directly determine this pressure, and the accepted estimates of $1{\cdot}1 \times 10^{10}$ dynes require to be multiplied by 41.

If the intrinsic pressures, as now suggested, are exactly determined by the heat of neutralisation, the value of the unknown term dp/dT in the Clausius equation $dp/dT = -L/\{T(v_2 - v_1)\}$ can be calculated. Moreover, if the Eötvös formula be true, namely, $\sigma(M/\rho)^{\frac{2}{3}} = K(\theta - 6)$, the surface tension of a single molecule is obtainable with the weight of the molecule or molecular aggregate, and as the periodic specific volumes and the periodic specific entropies of the elements are measurable they can all be shown to be functions of the atomic shapes, which recur in accordance with the periodic table when the chemical atoms are built up symmetrioally with the ether atom as the tetrahedral unit.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 258).

The Determination of Gallium alone, and of Gallium, Indium, Zinc, and Aluminium in the presence of One Another.

The Determination of Gallium.

Lecoq de Boisbaudran determined gallium by adding to a solution of a salt of gallium an excess of ammonium hydroxide and then boiling the solution until it turned litmus-paper red (*Ann. Chem. Phys.*, 1884, [6], ii., 181). This precipitated the gallium as the hydroxide, and Boisbaudran stated that the presence of salts of the alkali metals or of the alkaline earths did not affect the results. From 1 to 1·5 mgrm. of gallium per litre of solution was, however, unprecipitated.

Trial was made of this method of Boisbaudran by adding ammonium hydroxide to a solution of gallium chloride that contained about 0·05 grm. of gallium oxide. The solution was then boiled, and it was found necessary to continue the boiling for from thirty to forty-five minutes to effect the removal of the excess of ammonium hydroxide. Although the precipitate of gallium hydroxide was somewhat granular much of it adhered to the sides of the beaker and could not be detached. Another portion of the solution of gallium chloride was precipitated by ammonium hydroxide after ammonium chloride had first been added. The precipitate in this case was somewhat more gelatinous, but a portion of it adhered firmly to the sides of the beaker.

Because of this difficulty two other precipitants were next tried, and to render it possible to ascertain the accuracy of these new methods a solution of gallium of known concentration was prepared from some of the gallium chloride that had been purified by distillation. A sample of this gallium chloride was dissolved in water, an excess of ammonium hydroxide was added, and the resulting gallium hydroxide was washed, dried, and ignited to gallium oxide over a Bunsen flame. This oxide was then pulverised in an agate mortar, was reheated, and was then cooled in a stoppered weighing bottle. 0·6471 grm. of this oxide was heated with 1·5 cc. of concentrated sulphuric acid, the resulting gallium sulphate was dissolved in water, and the solution was diluted to 250 cc. in a measuring flask. This flask was calibrated to hold ten times the volume of a 25 cc. burette that wss subsequently used to measure portions of the solution.

The first reagent that was used for the precipitation of the gallium was sodium trinitride, NaN_3.

Precipitation of Gallium Hydroxide by Sodium Trinitride.—Portions of 25 cc. each of the slightly acid solution of gallium sulphate just described were diluted to about 250 cc. Solid sodium trinitride was added to each solution, and the solutions were then vigorously boiled for various lengths of time. The resulting precipitates of gallium hydroxide, which settled well, were collected on ashless filters, and were washed, dried, and ignited to gallium oxide over a Bunsen flame. The oxide was in each case ignited in a porcelain crucible, was cooled in a desiccator, and was then quickly weighed.

In determination No. 3, in which the boiling was continued for ten minutes, the precipitate adhered somewhat to the sides of the beaker, and this explains the low weight of gallium oxide. When the solution was boiled for a shorter time, Nos. 1, 2, and 4, the results were fairly satisfactory in each case, and the presence of as much as 15 grms. of ammonium chloride did not affect the accuracy of the method. The use of sodium trinitride, however, is open to two objections: the powerful physiological action of the hydronitric acid that is liberated when the solution is boiled, and the difficulty of obtaining on the market a supply of sodium trinitride of satisfactory purity. For these reasons sodium sulphite was substituted for sodium trinitride.

Table V.—*Precipitation of Gallium Hydroxide by Sodium Trinitride.*

	1.	2.	3.	4.
Weight of Ga_2O_3 taken (grm.) ..	0·0647	0·0647	0·0647	0·0647
Weight of NaN_3 added (grm.) ..	0·5	0·5	0·5	0·5
Time of boiling (minutes)	1—2	5	10	4
Other salts added..	None	None	None	5 g. NH_4Cl
Weight of Ga_2O_3 found (grm.) ..	0·0650	0·0660	0·0623	0·0657

Precipitation of Gallium Hydroxide by Sodium Sulphite.—A portion of the same solution as was used above was precipitated by adding about 1 grm. of solid hydrated sodium sulphite to the solution and boiling for four minutes. The precipitate was easily collected by filtration, but ignition to the oxide showed that precipitation had not been complete. 0·0784 grm. of gallium oxide was present in the solution, and the precipitate weighed 0·0728 grm. A further small amount of sodium sulphite was added to the filtrate, which was again boiled, and the precipitate yielded on ignition 0·0054 grm. of gallium oxide. In the precipitation of further portions of the solutions 1·5 grms. of sodium sulphite was added in each case. The results are given in Table VI.

The results are quite satisfactory even when fairly large amounts of ammonium salts are present. It was found that the solutions could be boiled for a much longer time

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

than when sodium trinitride was used, without causing the precipitate to adhere to the walls of the beaker.

TABLE VI.—*Precipitation of Gallium Hydroxide by Sodium Sulphite.*

	1.	2.	3.
Weight of Ga_2O_2 taken (grm.)	0·0647	0·0647	0·0647
Time of boiling (mins.)	10—12	6—7	7
Other salts present (10 grms.)	NH_4Cl	NH_4NO_3	$(NH_4)_2SO_4$
Weight of Ga_2O_3 found (grm.)	0·0649	0·0661	0·0641

A slight modification of this method of precipitation, which avoids the introduction of sodium salts into the solution, was later employed in the determination of gallium in a sample of cæsium gallium selenate alum (see *prox.*). A solution of ammonium sulphite, which was prepared by saturating ammonium hydroxide with sulphur dioxide, was substituted for solid sodium sulphite. A value of 13·33 per cent of Ga_2O_3 as against a calculated value of 13·31 per cent in the alum was obtained.

In making weighings of gallium oxide it was observed that this substance, like the oxides of aluminium and indium, is quite hygroscopic, and in all of the analyses that are later described the crucible that contained the gallium oxide was placed in a stoppered weighing bottle as soon as it was removed from the desiccator, and was weighed in that bottle.

In the determinations of gallium described below gallium was precipitated by sodium sulphite, the procedure being as follows:—If ammonium chloride or hydrochloric acid is not already present in the solution, a few cc. of hydrochloric acid is added, the solution is then made slightly alkaline with ammonium hydroxide, and about 1·5 grms. of hydrated sodium sulphite is dissolved in the solution. This weight of sodium sulphite suffices for the precipitation of 0·1 grm. of gallium oxide, and the amount of gallium should usually not be permitted to exceed this amount because otherwise the precipitate of gallium oxide is so bulky as to render difficult its filtration and washing. After the sodium sulphite has been dissolved in the solution hydrochloric acid is carefully added until the solution is distinctly acid to litmus-paper. The solution is then vigorously boiled for about six minutes. The resulting precipitate of gallium hydroxide is allowed to settle, and is then filtered on an ashless filter-paper and washed until the wash water is free from chlorides. The precipitate is dried and is ignited with the paper over the Bunsen flame in a porcelain crucible. The crucible is placed in a desiccator while still warm, and is afterwards transferred to a stoppered weighing bottle for weighing.

The precipitation of gallium by this method is usually complete, but it nevertheless is advisable to add a small amount of sodium sulphite to the filtrate, and to boil that for some minutes to ascertain whether gallium is present. If insufficient hydrochloric acid was added before the solution was first boiled some gallium may be retained in solution by the alkali resulting from the hydrolysis of the sodium sulphite. To guard against this error the filtrate, after boiling with a small amount of sodium sulphite and the removal of any precipitate that may form, should be acidified with acetic acid and boiled for twenty minutes. Any gallium hydroxide that appears on this treatment is collected, ignited, and weighed, and its weight added to that of the oxide already obtained.

Precipitation of Zinc as Zinc Mercuric Thiocyanate from Solutions that contain Gallium.

Zinc forms a difficultly soluble double salt with mercuric thiocyanate. Gallium does not. To ascertain whether this fact could be utilised to separate zinc from gallium, a solution that contained the sulphates of gallium and zinc was made slightly acid with sulphuric acid, and an excess of a solution of potassium mercuric thiocyanate was added. After several hours the precipitate of zinc mercuric thiocyanate was removed by filtration. The filtrate was treated with hydrogen sulphide to precipitate the mercury, the mercuric sulphide was filtered off, the filtrate was boiled to remove hydrogen sulphide, and ammonium hydroxide was then added until the solution was slightly alkaline. Acetic acid was next added in slight excess, and the gallium that was present was precipitated as the hydroxide by boiling this solution. This hydroxide was dissolved in a slight excess of sulphuric acid, the solution was diluted to 100 cc., and the metals in the resulting solution were fractionally deposited by electrolysis on a rotating platinum rod, using a current of 2 to 3 ampères. Spectroscopic examination of the deposits on the cathode showed that zinc and gallium were present in all of them, zinc predominating in the early fractions and gallium in the later ones. These results showed that zinc was not completely precipitated by potassium mercuric thiocyanate under the conditions above described.

While this work was in progress, however, an investigation of this method for the determination of zinc was completed in this laboratory by Mr. C. S. Hoyt (see Note) working under the direction of Prof. G. E. F. Lundell. These investigators established the conditions under which the precipitation of the zinc should be made, and careful observance of their directions gave us very satisfactory results.

(NOTE.—"The Zinc Mercuric Sulphocyanate Method for the Determination of Zinc," a thesis presented to the Faculty of the Graduate School of Cornell University, June, 1917; also Lundell and Bee, *Trans. Am. Inst. Metals*, Sept., 1914).

The reagent is prepared by dissolving 27 grms. of mercuric chloride and 39 grms. of potassium thiocyanate in 1 litre of water. The solution of the zinc salt to be precipitated should not contain more than 0·1 grm. of zinc in 200 cc., and this volume of solution should contain about 2 cc. of concentrated nitric acid or sulphuric acid. The solution of potassium mercuric thiocyanate is added by drops to the solution of zinc, which is constantly stirred during the addition of the precipitant. In making a determination of zinc the reagent is added until a precipitate begins to form, and from this point 20 cc. of the precipitant is added for every 0·1 grm. of zinc estimated to be present. After precipitation is complete the contents of the beaker are allowed to stand for several hours. The precipitate is then collected in a Gooch crucible, is washed with water that contains 20 cc. of the reagent per litre, and is then dried at 105—110°. The zinc factor for this precipitate is 0·1314.

The accuracy of the separation of zinc from gallium by this improved method was tested by precipitating the zinc from a slightly acid solution containing known amounts of zinc and gallium. After the precipitate of zinc mercuric thiocyanate had been removed by filtration 10 cc. of hydrochloric acid was added to the filtrate and the mercury in the solution was precipitated by hydrogen sulphide. The mercuric sulphide was filtered off, the filtrate was boiled to expel hydrogen sulphide, and the gallium was then thrown down by sodium sulphite (see above), and was weighed as the oxide. The results of two analyses, which are given in Table VII., show that the method is quite satisfactory for the determination of zinc and gallium in the presence of each other.

TABLE VII.—*The Separation of Zinc from Gallium.*

	1.	2.
Weight of zinc taken (grm.)	0·0939	0·0939
Weight of zinc found (grm.)	0·0929	0·0937
Weight of gallium oxide taken (grm.) ..	0·0828	0·0828
Weight of gallium oxide found (grm.) ..	0·0823	0·0830

(To be continued).

INDUSTRY AND HIGHER EDUCATION.

A MEETING was held on Tuesday, May 20, between representatives of the Universities and Colleges and representatives of the Federation of British Industries.

Sir RICHARD VASSAR-SMITH, Bart., presided over the gathering, and in his introductory remarks stated that the meeting had been called to consider the setting up of an organisation which might act as a clearing house between Universities and the Industries of the country.

It was desired to make some arrangements by which young men leaving the Universities would have the opportunities of passing into productive work, which would give full scope to their abilities and education. Such an organisation should enable the man of real merit to obtain a post which would allow him to use his abilities to the fullest extent.

Personally he felt there was need of such an organisation, as in the future it would be more imperative than ever that each man, in whatever grade, should be working efficiently. There was a need in industry for a supply (and the maintenance of that supply) of the best intelligence of the country. It was in order to discuss this question that the meeting had been called.

Mr. H. A. Roberts, of Cambridge University, stated that the suggestion was one which would meet with approval by all interested in national wellbeing. There were difficulties in setting up such an organisation, and it might be advisable in the first case to limit the activities until further experience had been gained. It was very undesirable to innovate a scheme on too grand a scale until experience had been obtained.

Prof. Ferrier, of Bristol University, pointed out that there had been no difficulties in placing the really first-class men, but men of the second class certainly needed assistance. In many cases the second-class men had made good when they had been able to obtain a position which offered scope; ability was not confined to academic distinction; especially was this the case in regard to work in Industry and Commerce. As a rough estimate he would say that 5 per cent of the first-class University men would be required for research purposes. The remaining 95 per cent would be employed as ordinary routine business men. There had been a marked tendency for the University trained men to proceed overseas, and even in the United States the English University man was generally sure of finding employment. It was to be hoped that this exodus of the finer grade of worker would be stopped by the offer of suitable employment in this country.

Prof. Baker, of the Imperial College of Science and Art, stated that he was in full agreement with the last speaker, and that the real difficulty was in fixing the second grade student, although there must really be a demand for them. In the chemical industry, for instance, there was routine work which would be more ably carried out by the trained man. In most cases, at present, this was carried out by the ordinary worker. The value of the well trained man in routine work was not appreciated at present, and he hoped that by the scheme which had been outlined the Employer would eventually come to the Organisation for such men besides the super-men of research.

Prof. Lea, of Birmingham University, hoped that the scheme would include all grades of men. Industry needed all grades, and education could never hope to produce men of one grade only. He thought the Federation, being such a thoroughly representative body, could best tackle this scheme, which he felt would encourage closer co-operation between the University and Industry.

The Master of Pembroke College, Cambridge, stated that there had been a great increase in the number of employers who were now sending their sons for University training; this was an excellent sign, and should help eventually in obtaining the co-operation for which Prof. Lea hoped.

Prof. Bulleid, Nottingham University, hoped that the institution of such an organisation would not mean putting another barrier between the student and the possible employer; he had always found that the most satisfactory method for obtaining posts was for the student to write to the employer direct.

Dr. R. A. Duff, of Glasgow University, suggested that it might be found that centralising vacancies in the proposed Clearing House might be the best way of tackling the problem. This was a question of administration and would no doubt be considered before fully settling the scheme.

Miss M. H. Mead, of Manchester University, asked whether the organisation would deal with women. In reply it was stated that the term "students" had been expressly used in the Memorandum as meaning to convey that both men and women were included in the scheme.

It was decided that a further meeting should be held to thrash out practical points for the setting up of the scheme at an early date.

The meeting was attended by representatives of the Universities of Birmingham, Bristol, Cambridge, Durham, Glasgow, London, Manchester, Oxford, Sheffield, Wales, and the Imperial College of Technology and the University College of Nottingham.

Letters had been received from Queen's University, Ireland, and Liverpool University, expressing their sympathy with the scheme, and regretting their inability to be represented at the meeting.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 22, 1919.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"*On the Structure of Lysorophus as Exposed by Serial Sections.*" By Prof. W. J. SOLLAS, F.R.S.

As the precise position of Lysorophus, regarded by Broom as the most interesting vertebrate fossil discovered for many years past, still remained open to discussion, some nodules containing its remains were placed in my hands for investigation by serial sections.

This work is now complete, and all the facts of the anatomy of the skull and vertebræ, and the main features of the shoulder girdle and fore limbs are exposed with a precision and wealth of detail only otherwise to be looked for in a recent skeleton.

It is now placed beyond question that Lysorophus belongs to an ancestral group of amphibians closely related to the Urodela.

Among the striking primitive characters it retains may be mentioned the presence of a basi-occipital and a supra-occipital bone, with a foramen in the former for the xiith nerve, and possibly connected with this the presence of a large paired proatlas. There is also a separate opisthotic, and a pair of pillars, recalling the epipterygoids of the Chelonia, which may provisionally be termed ali-sphenoid.

The condylar articulation of the skull is of particular interest; while all the other vertebræ are amphicœlous, the first is opisthocœlous and is swollen in front into an odontoid process, which plays against the nearly flat posterior face of the basi-occipital. The ex-occipitals are seated in part on the basi-occipital and in part on the first vertebra, thus forming with the basi-occipital a hollow joint (opisthocœlous) in contrast to the procœlous articulation of the reptilia.

The arch of the first vertebra and the face of the proatlas are closely applied to the back of the skull in a manner which recalls many fishes.

The hyoid (hypohyal and ceratohyal), and the branchial arches (cerato-branchial and epibranchial) are large and well ossified. The number of the branchial arches is at least three, more probably four.

"*A Preliminary Study of the Energy Expenditure and Food Requirements of Women Workers.*" By O. ROSENHEIM.

Direct determinations (by the Douglas-Haldane method) of the energy expenditure of women were made during periods of rest, recreation, and work, the latter referring to work on the lathe. By means of the data obtained, an approximate estimate of the daily food requirements, expressed in calories, was arrived at on the basis of certain considerations set forth in the communication. The results agree with those of previous workers obtained by indirect statistical methods.

"*Report on the Metabolism of Female Munition Workers.*" By M. GREENWOOD, C. HODSON, and A. E. TEBB.

Observations were made upon 43 women engaged upon 12 different processes in the manufacture of projectiles, the rate of metabolism being determined by the method of indirect calorimetry. Making the allowance for metabolic needs during non-working hours recommended by the Royal Society Food (War) Committee, the workers were found to fall into four classes, for each of which the daily requirements per average woman were 2530 calories, 2810 calories, 3200 calories, 3425 calories. The results were concordant with the inferences drawn from a study of food consumption in a large explosives supply factory during the war. The figures obtained in this experimental work were somewhat larger than those reached by Becker and Hämäläinen.

GEOLOGICAL SOCIETY.

Ordinary Meeting, May 7, 1919.

Mr. G. W. LAMPLUGH, F.R.S., President, in the Chair.

THE PRESIDENT said—Major R. W. Brock, formerly Director of the Geological Survey of Canada, was called upon last year to undertake on behalf of the War Office an arduous journey in Palestine, during which he had to devote particular attention to the Dead Sea region. At the request of the Officers of the Society, Major Brock has kindly undertaken to tell us something of his observations in the country. It is needless to say that the region is of surpassing interest to geologists, and I am sure that the Fellows will appreciate the opportunity of hearing how its remarkable features have impressed so acute and experienced a field-geologist.

Major REGINALD W. BROCK, M.A., F.G.S., then proceeded to deliver his lecture on the Geology of Palestine, his observations being summarised as follows: -

The following formations are recognised—

QUATERNARY.

Alluvium. Dunes; Valley and Plains clay, and Silt; Desert Crust.

Diluvium. Terrestrial: Lisan Formation (Jordan-lake-beds).

Marine: Upper Calcareous Sandstone and Limestone. Lower Calcareous Sandstone.

Heavy volcanic flows, basalts, ashes, tuffs, &c.

TERTIARY.

Pliocene. Lacustrine.

Eocene. Nummulitic Limestone.

MESOZOIC.

Cretaceous. Upper: Senonian (Danian; Campanian; Santonian); volcanics, basalts.

Lower: Nubian Sandstone; Jebel-Usdum formation (?)

Jurassic. On Lebanon and Hermon only.

PALÆOZOIC.

Carboniferous. Possibly south-east of the Dead Sea.

Cambrian. Dolomite and sandstone.

PRE CAMBRIAN.

Volcanics and arkose.

Red granites and porphyries.

Grey granites, gneiss, and crystalline schists.

The structure was shown to be that of a tableland bisected by a great rift-valley (graben), and flanked by a coastal plain. A section was exhibited illustrating East Jordanland acting as a horst; the boundary-faults of the Jordan Trench; the unequal sinking of the contained blocks; the western section of the tableland sunken with relation to the eastern, and thrown into an asymmetric anticline, the limbs of which rise in steps through monoclinal flexures or faults.

Lantern-slides were used to illustrate the character of the country and outstanding features in its geology, more particularly the following:—The dependence of the topography upon geological structure, slopes depending on the attitude of the rocks and elevation upon the raising or depressing of fault-blocks or on lava-flows; basins and sunken areas in the tableland; the scarps bounding the Jordan Trench, especially the western fault and fault-blocks in the Trench or against its walls that have not sunk equally with others; the upturned block of Jebel Usdum which, with the Dead Sea bottom and the block nort of Jericho, indicates a median fault between the boundary-fault; the interbanding of the Jebel-Usdum salt with sandstone and shales that resemble Nubian Sandstone; the unconformity of the Jebel-Usdum formation with the Jordan lake-beds (Lisan formation), which with the chemical composition of the salt (lack of bromine, &c.) shows that it is not a Jordan lake deposit; high lake-terraces in the centre of the Trench, with corresponding ones north of Tiberias and south in the Araba Valley, showing that the Jordan lake stood 1400 feet above the present Dead Sea, and that there has been no marked warping since their formation; old gravel-filled cañons of the Arnon and Terka Main which prove that the level of the Dead Sea before Jordan-lake days stood at about its present level, and that climatic conditions must have been about the same, also that it did not long precede the Jordan lake; the Lisan formation of the Jordan lake-beds, thin layers of mechanical and chemical sediments veneered along the Jordan river with fluviatile clays; bad-land topography near the wadis and in the Lisan formation: narrow box cañons of the wadis in the Jordan Trench and the more open valleys above producing a sort of "hanging valley."

In the main, Blanckenhorn's recent work was confirmed, in particular the fault forming the western border of the Trench and disturbances and sinking in the tableland; but new points were mentioned, such as the evidence of a median fault within the Trench; the sea-cliffs of Lisan and Jebel-Usdum; the wave-cut shelf and the salf of Jebel-Usdum; the tilting of the Jebel-Usdum block and its independence from and unconformity with the old lacustrine beds; lack of disturbance and of warping since their deposition; the age and former level of the Old Dead Sea and the recent rise in the present sea, the latter indicating an increase in moisture and not drier conditions as generally supposed.

A vote of thanks was unanimously accorded to Major Brock for his lecture.

ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on June 2. Sir James Crichton-Browne, F.R.S., Tresurer and Vice-President, in chair. Captain Ralph A. Bagnold, Mrs. Charles Cave, Mr. Edmund Davis, J.P., Miss Amelia D. Defries, Mr. William E. Schall, and Mr. Frank Twyman were elected members.

NOTES.

An interesting paper on the "Occlusion of Hydrogen by the Metallic Elements," by Donald P. Smith, is given in the *Journal of Physical Chemistry* for March, 1919. The results of a very complete search of existing literature are embodied in tabular form, and the conclusion of the author that the capacity of a metal to occlude hydrogen is connected with its magnetic character is best given by the Summary that follows the paper:—"From a review of the literature relating to the occlusion of hydrogen by the metallic elements it is shown that the resulting alloys are clearly to be distinguished from other types of binary hydrogen compounds, and that the metals which form the alloys probably occupy a definite region in the periodic table of Werner. The metals of this region are classified into those which do, and those which do not, occlude in a degree measurable by the ordinary volumetric method. From a comparison with magnetic data it is shown that the occluding and non-occluding elements, excepting copper, rhodium, and thorium, are identical with those for which the specific magnetic susceptibility possess a value respectively greater or less than about $+0{\cdot}9 \cdot 10^{-6}$ at room temperature. It is concluded that the capacity of a metal to occlude hydrogen in large degree is an accompaniment of strongly magnetic character."

The "Tank."—We are indebted to Major-General E. D. Swinton for an account of the origin of this contrivance about which so much has been said and written, and which undoubtedly contributed largely to the successful termination of the war. The account was given at an informal dinner following the general meeting of the Institute of Mining and Metallurgy on April 10 last. We quote the Major's own words:—"In July, 1914, Mr. Marriott wrote from Antwerp—where his job at the moment was trying to find out some cheap and efficient form of transport across rough country for mining purposes. He knew all about rope railways, telpherage, narrow-gauge railways, and so on, and informed him that in Antwerp he had seen an American caterpillar tractor which would go over rough country and climb 'like hell.' This, it must be remembered, was before the war. He (General Swinton) happened to be in a position then when he could approach different departments; in vulgar language he was a sort of Buttinski, and he was able to go to the War Office and the Admiralty and tell the people concerned that there was an American tractor in Antwerp which would, in the coarse words of his friend, 'climb like hell,' and that it was up to them to investigate it for tractive purposes. The machine referred to was the Holt tractor. Shortly after that he had gone out to the war, as he had said just now, as a journalist, and his position gave him an opportunity of seeing and learning a lot. It was then that he became convinced that a machine which could climb like hell was a thing not to be lost sight of, and if it could be developed or improved into a bullet-proof machine which could climb 'to beat hell' they had something which might meet the German machine guns."

At a recent meeting of the Society of Public Analysts and other Analytical Chemists a paper was read by Helen Masters, B.Sc., on "Soluble Lead in the Glaze of Casseroles." Attention was drawn to the extended use of glaze vessels for culinary purposes and to the danger that food cooked in such vessels might become contaminated with lead. In Germany the sale of vessels which yield any soluble lead on boiling for thirty minutes with a 4 per cent solution of acetic acid is prohibited. Experiments with various glazed vessels show that in some cases a considerable amount of lead can be extracted from the glaze, not only by the action of 4 per cent acetic acid, but also by the action of more dilute solutions of organic acids, *e.g.*, 1 per cent acetic, citric, or malic acid. In some cases as much as from 2 to 4 mgrms. of lead monoxide per square decimetre was extracted by a 1 per cent acetic acid solution in thirty minutes, and in an exhaustive experiment of this kind as much as 28·7 mgrms. of lead monoxide per sq. dem. was extracted by twelve successive boilings. The danger of the use of such vessels is very real, and manufacturers would do well to have reliable tests made of their wares so as to avoid the use of soluble glazes; the expense would probably be well repaid by marking their wares with a guarantee of their insolubility.

We have received a copy of the first number of a new publication, the *Italian Gazette*, a financial, commercial, and economic review, a quarterly journal, edited by Roberto Lombardo, with Edward Storr, as sub-editor; published at Piazza Cavour 17, Rome. The matter opens with a message of appreciation from the British Ambassador, Sir Rennell Rodd, and the object is to improve and strengthen the relations of sympathy and friendship between England and Italy that have become so apparent during the War. In a brilliant introductory article by Luigi Luzzatti the need for an intimate friendship between Italy and England is developed. Other articles on financial and commercial matters by prominent Italians appear, and in all of them there is to be noticed a sincere desire for the friendly relations between us to be expanded for our mutual benefit, and an avowal of their distrust of Teutonic methods in commercial and other circles that has been brought home to them as to other nations by recent developments. We wish the new publication every success. Our only regret is that it is not to appear at more frequent periods than once a quarter.

NOTES FROM FOREIGN SOURCES

Stability of Javel Extracts.—M. Fonzes-Diacon.—Javel extracts, when kept, lose considerable quantities of active chlorine, the loss being caused principally by the action of light and the author has made a study of the course of the reaction and the conditions which may lead to its reduction to a minimum. Eight samples were exposed to the action of diffused light by putting them before a well lighted window on which direct sunlight was not falling; two were placed in flasks made of yellow glass, one of a much darker shade than the other, and the six others in white glass. The chlorine was determined at intervals of time extending over about four months, and it was found that even in that time the loss of chlorine in the dark yellow flask was very small; in the less deeply coloured glass it was rather greater and still more marked in the white flasks. The greater the proportion of active chlorine the greater the loss, and after four months' exposure to the action of light extracts which originally contained very different amounts gave results which approached a common limit. If the initial amount of active chlorine present is about 5 grms. per 100 cc., and if the extracts are kept in dark yellow flasks, they may be regarded as unaltered at the expiration of several months. —*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 206.

Analysis of Antimony Salts.—Various methods have been suggested for the analysis of antimony sulphide, which may contain free sulphur, antimonic acid, antimonates, red antimony sulphide, antimony oxysulphides, or calcium sulphate. The oldest methods of determining the amount of free sulphur depended upon the extraction of it by carbon disulphide, using a Soxhlet's apparatus, and it has recently been found that the pentasulphide is practically unattacked in the cold, and even on warming only about 0·4 per cent is reduced. Benzene or acetone can be used as solvent, but if benzene is used the pentasulphide must previously be thoroughly dried. Acetone is not to be recommended, for it dissolves a small quantity of the sulphide in addition to the free sulphur. Another

method of determining the impurities depends upon the fact that antimony pentasulphide is completely soluble in warm ammonia, and the other substances present can be filtered off and determined in the usual way. To estimate the total sulphur the sulphide can be dissolved in a solution of pure potash and then subjected to the action of chlorine, when all the sulphur is transformed into sulphuric acid and the antimony into antimonic acid. Fuming nitric acid can also be used to convert the sulphide into sulphate, which can be estimated as barium sulphate in the usual way, and hydrogen peroxide acts similarly. If the sulphide is dissolved in pure sodium sulphide the percentage of antimony present can be determined by electrolysis, platinum electrodes being employed; but this process cannot be recommended, for the values obtained are always too high. By treating a solution of the sulphide with soda and hydrogen peroxide and adding alcohol, a precipitate of sodium antimonate is obtained after thirty-six hours' standing. From the weight of this precipitate the amount of antimony present can be deduced. In an alternative process the antimony is determined as tetroxide, Sb_2O_4. A given weight of the sulphide is heated over a water-bath with hydrochloric and nitric acids. The solution is evaporated to dryness, taken up with hydrochloric acid, diluted, and filtered. The precipitate consists of silica and calcium sulphate. The antimony is contained in the filtrate, which is decomposed by HCl, and oxidised to give Sb_2O_4.—*Revue des Produits Chimiques*, 1919, xxii., 199.

Determination of Arsenic in Volatile Cacodylic Compounds. – L. C. Maillard.— Cacodyl and its compounds readily combine with oxygen to give cacodylic acid, which is a very stable derivative in ordinary conditions. It is non-volatile, has no smell, and is not toxic. For the purposes of analysis the best oxidising agent to use is persulphuric acid, employed in the form of ammonium persulphate. To extract the arsenic from the cacodylic acid the latter is attacked with a mixture of nitric and sulphuric acids, the excess of nitric acid is driven off by heating, and the arsenic is precipitated in the diluted solution as sulphide, and weighed either as sulphide, or as arsenic acid, or as magnesium pyroarsenate. Even in the case of a long series of operations, when an accumulation of errors might be feared, the author has found by a control experiment that this method gives excellent results in determining arsenic in volatile substances of the cacodyl series, and it is possible that it may be applicable to the case of other organic compounds containing arsenic of more or less comparable composition.—*Bull. Soc. Chim. de France*, 1919, xxv.-xxvi., 192.

MEETINGS FOR THE WEEK.

Saturday, June 7.

Royal Institution, 3. "The Italian Front," by J. M. Price.

Wednesday, June 11.

Conjoint Board of Scientific Societies, 5. (At Royal Society, Burlington House).

Thursday, June 12.

Royal College of Physicians, 5. (Croonian Lecture). "The Significance of the Cerebral Cortex," by Prof. C. Elliot Smith.

Friday, June 13.

Physical Society, 5. "Comparison of the Wave-form of the Telephone Current produced by a Thermal Detector and a Rectifier in the Heterodyne Reception," by V. van der Pol. "Magnetic Properties of Varieties of Magnetite," by E. Wilson and E. F. Herroun.

Saturday, June 14.

Biochemical Society, at Rothamsted Experimental Station, Harpenden.

Chemist, demobilised, three years' Technical College training and one year works experience, in order to regain experience, lost Army service, would communicate with Analyst of extensive practice with view to Post as Pupil Assistant for limited period.—Address, R. B., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

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THE CHEMICAL NEWS

VOL. CXVIII., No. 3087.

RESEARCHES IN OPTICAL ACTIVITY.*

PART I.—THE TEMPERATURE-ROTATION CURVES FOR THE TARTRATES AT LOW TEMPERATURES.

By T. S PATTERSON, D.Sc., Ph.D., Waltonian Lecturer and Lecturer in Organic Chemistry, University of Glasgow, and
K. L. MOUDGILL, B.Sc, late Robert Donaldson Scholar, University of Glasgow.

IN some previous papers by one of the present authors it has been shown, by piecing together evidence obtained in various ways, that if the rotation of such a substance as

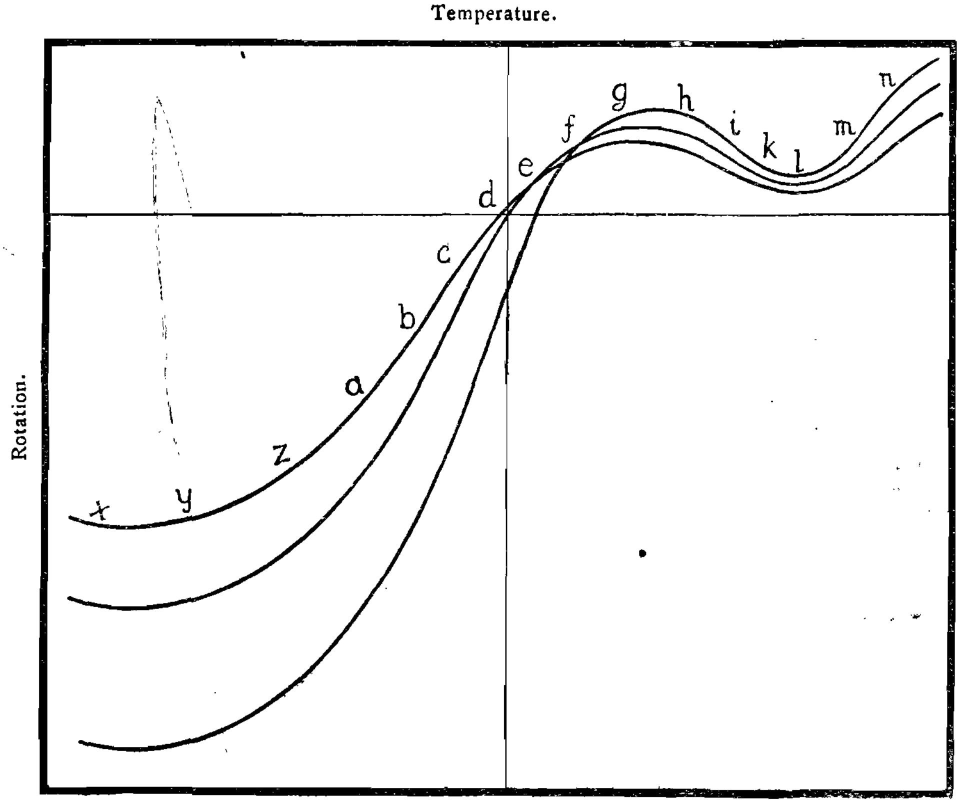


FIG. 1.—General Temperature-Rotation Curves for Tartrates.

ethyl tartrate could be examined for different colours of light over a sufficiently wide range of temperature, the graphs would have the appearance shown in Fig. 1; they have been traced up to the present from about the region *a* to the region *n*. In the paper now submitted an attempt has been made to follow the trend of these T—R curves towards low temperatures, adopting the same method as before. In the following experiments a start has been made in this direction, but before passing on to our primary purpose we thought it worth while to investigate one rather striking instance of solvent effect connected with the high temperature end of the diagram. It has been shown by Walden (*Ber.*, 1905, xxxviii., 371) that cinnamic aldehyde has a very marked effect upon the rotation of ethyl tartrate and of methyl malate, the mere numerical values being greater than those recorded for either of these active substances in any other solvent, on which account we were anxious to ascertain whether the behaviour in the former case fitted in with the views previously developed or not.

A solution of ethyl tartrate in cinnamic aldehyde, $p=9{\cdot}64$ ($p=$grms. active substance per 100 grms. of solution), was therefore prepared, and the rotation examined for six colours of light. Three of these, *yellow*, *green*, and violet, were obtained direct from a mercury arc lamp, whilst the other three, dark red (r_1), red (r_2), and blue, which correspond to three fainter lines in the mercury arc, were obtained from a Nernst lamp by a method which has been described elsewhere (*Journ. Chem. Soc.*, 1916, cix., 1144). The wave-lengths of the light used were as follows:—

r_1	r_2	y	g	b	v
6716·3	6234·3	5790·3	5460·7	4959·7	4358·3

It will be noticed that the rotations at low temperatures are great, and that as the temperature rises the rotation diminishes, which was in accordance with expectation. The T—R curves for this solution are shown in Fig. 2, and are there contrasted with those for ethyl tartrate in quinoline $p=13{\cdot}601$ (*Journ. Chem. Soc.*, 1916, cix., 1145, 1151). The curves are, on the whole, similar, but those for the cinnamic aldehyde solution lie higher on the diagram than those for the quinoline solution. In quinoline a minimum is apparent, but in cinnamic aldehyde the curves are only tending towards a minimum, which would lie at a distinctly higher temperature than could, meantime, be reached. Now

* Abridgment of a paper in the *Proceedings of the Royal Society of Edinburgh*, 1918-19, xxxix., 18—34.

it has been suggested in recent papers that the influence of a solvent should be measured, not so much by the actual value of the rotation in given circumstances, as by the effect which the solvent produces on the whole family of T—R curves. If this be so—and there is much evidence in favour of the idea—quinoline must be regarded as a more powerful solvent for this ester than is cinnamic aldehyde, since the shifting of the T—R curve is apparently much greater in the former than in the latter case, and it is at least quite possible, indeed it is very probable, that if the quinoline solution were examined at lower temperatures directly at low temperatures; but this procedure presents a number of difficulties such as the likelihood of solidification of the active substance or of the solvent, or the difficulty of obtaining and maintaining low temperatures. Secondly, the active compound may be dissolved in some solvent which brings into the region of ordinary temperatures the T—R curves, which, in the homogeneous substance, could only be directly observed at very low temperatures. Thus in the case of ethyl tartrate it has already been shown (*Journ. Chem. Soc.*, 1908, xciii., 360; Winther, *Zeit. Phys. Chem.*, 1907, lx., 578) that in

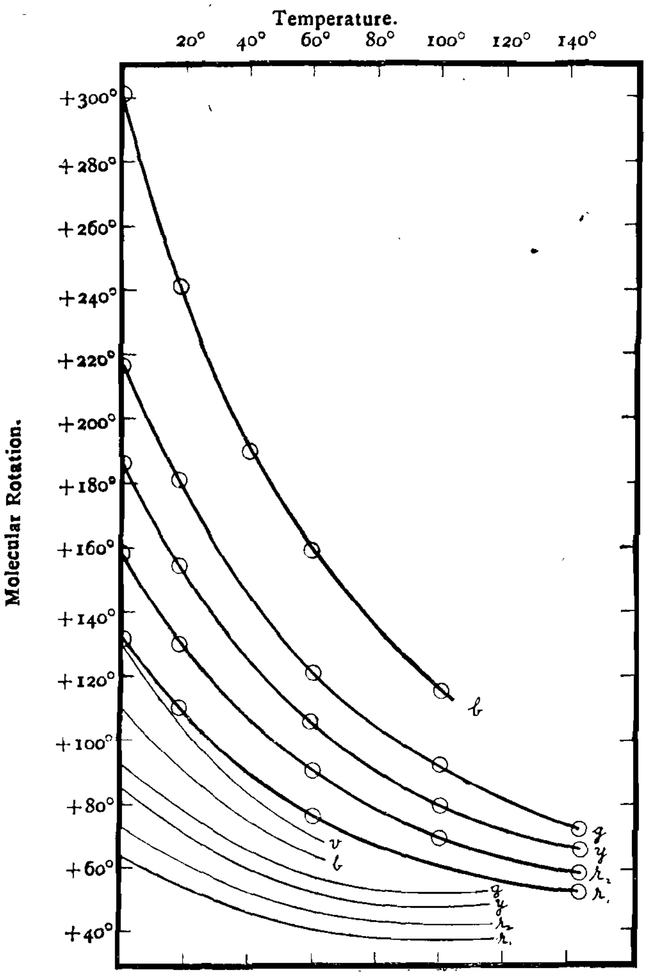


Fig. 2.—Temperature-Rotation Curves for Ethyl Tartrate in Cinnamic Aldehyde, $p = 9{\cdot}64$ (heavy lines), and in Quinoline, $p = 13{\cdot}601$ (thin lines).

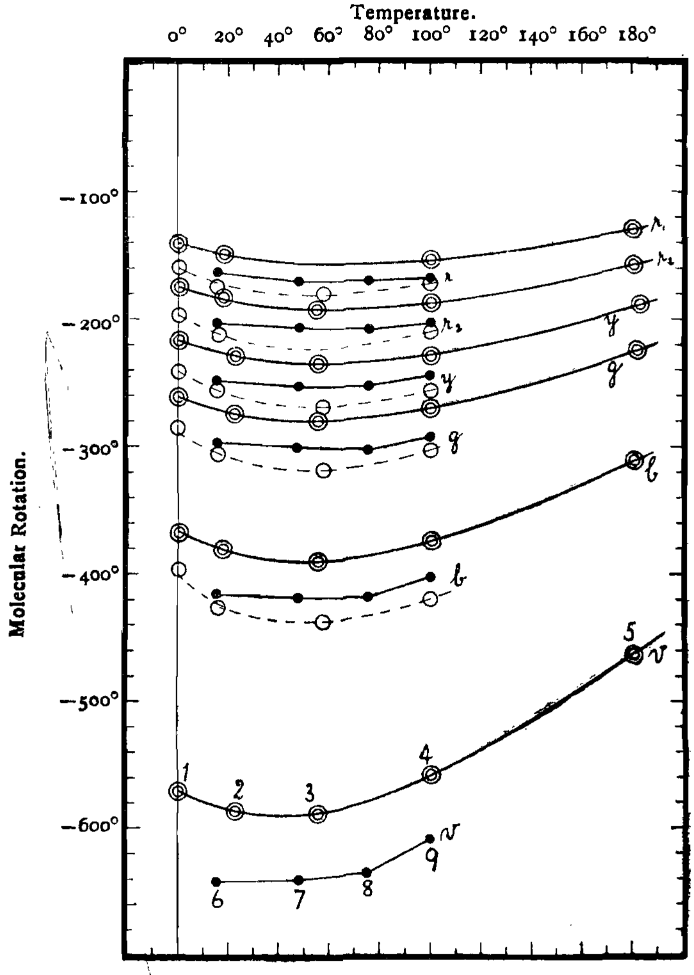
than those for which the diagram applies, the quinoline curves would rise to higher values than those for cinnamic aldehyde. This is also in agreement with the fact that whereas C—R (concentration-rotation) curve for ethyl tartrate in quinoline shows a pronounced maximum (*Journ. Chem. Soc.*, 1909, xcv., 322), Walden's results for ethyl tartrate in cinnamic aldehyde give only a very slight indication of the occurrence of this phenomenon in dilute solution.

We may now turn to the question with which this paper is primarily intended to deal, namely, the course of the T—R curves for tartrates at low temperatures. There are various ways of investigating the problem. Firstly, a substance, homogeneous or in solution, can be examined ethylene bromide the rotation is very considerably depressed, wherefore most probably, in this particular solvent, the whole T—R curve is displaced towards the right of the diagram—that is, in the direction of high temperatures; or, to put it otherwise, ethylene bromide brings into view, at the ordinary temperature, the part of the diagram *a b c* (Fig. 1), which, in homogeneous ethyl tartrate, could only be observed at decidedly lower temperatures. The behaviour of ethyl tartrate in ethylene bromide at moderate temperatures ought therefore to reveal the behaviour of the homogeneous ester at temperatures lower still. Thirdly, the behaviour of some related substance can be studied either in the homogeneous condition or in solution. Thus in passing from

ethyl tartrate to *iso*butyl tartrate—a slight change of constitution—the general T—R curves are slightly displaced towards the left, towards lower temperatures; whereas on converting ethyl tartrate into ethyl diacetyl tartrate—a considerable change of constitution—the displacement of the general T—R curves is very much greater and is in the opposite direction.

Applying, to begin with, the second of these methods, ethyl tartrate was examined in ethylene bromide solution. Unfortunately, in attempting to get readings at as low a temperature as possible, the solution was cooled rather too far, so that the solvent crystallised out and spoiled the experiment at an early stage. Nevertheless it was found that the rotation for violet is, in the absolute sense, very much lower than for the other colours examined, and that the rotation increases rapidly with rise of temperature, so that the effect of this solvent is very much the opposite of that of cinnamic aldehyde, whence it may be concluded that the former is represented by the part *b c* of the general curves (Fig. 1), whereas the latter is represented by the region *h i k*. But it is clear that the depressing influence of ethylene bromide is not sufficient to take us into a region of minimum rotation, and since ethylene bromide is either the most powerful, or almost the most powerful, depressing solvent known for this ester, we were forced to turn next to the third method of investigation, namely, that of examining the T—R curves of some other tartrate, in which there is reason to suppose that the change of constitution has brought about a considerable shifting of the family of T—R curves.

Now it has been shown by Frankland and Wharton (*Journ. Chem. Soc.*, 1896, lxix., 1587, also 1309) that the rotation, for yellow light, of ethyl dibenzoyltartrate exhibits a distinct minimum rotation at 60·4°; moreover, this rotation is low in value ($[\alpha]_D$ 18 = −59·36°), and it seems clearly possible that the T—R curves for this ester at ordinary temperatures represent the behaviour of ethyl tartrate—the parent ester—at very much lower temperatures. The examination of an active substance for a single colour of light can only yield an indication in regard to this question, but an examination of the T—R curves for various colours of light makes a definite decision possible. Thus if, for example, the minimum in ethyl dibenzoyltartrate correspond to the minimum which exists in ethyl



◎ Homogeneous.
○ In cinnamic aldehyde (p = 9·55).
● In ethylene bromide (p = 9·20).

FIG. 3.—Temperature-Rotation Curves for *iso*Butyl Dibenzoyltartrate in various Solvents.

tartrate at about 180°, namely, to the region *k l m* in Fig. 1, then we should expect the dispersion to be the same in both cases, namely, positive; the rotation for violet should be greater, in an absolute sense, than for red. But if the minimum were such as is to be expected *from a continuation* of the ethyl tartrate curves towards low temperatures, or for the curves for ethyl tartrate in ethylene dibromide, the rotation for red might be expected to have a higher absolute value than the rotation for violet, the dispersion then being negative. In this way it is possible to decide to which region of the ethyl tartrate curves those for ethyl dibenzoyltartrate correspond. Instead, however, of the ethyl derivative, we prepared *iso*butyl dibenzoyl-neighbourhood of zero rotation, the observed behaviour is, so far, in agreement with our views. It would obviously, however, be of interest to examine these curves towards the right-hand side of the diagram, and, in the hope of *being able to shift them far enough to link them up* definitely with those for ethyl tartrate or *iso*butyl tartrate, *iso*butyl dibenzoyltartrate was examined in ethylene bromide and in cinnamic aldehyde solutions, the curves obtained being also shown in the diagram in Fig. 3. But in this we were disappointed, for although the solvents altered the rotation to some extent, the change is not very great. In cinnamic aldehyde the general character of the curves appears to be almost the same as in the homo-

This Diagram is for Green and Violet, the Reference Colour being Green.

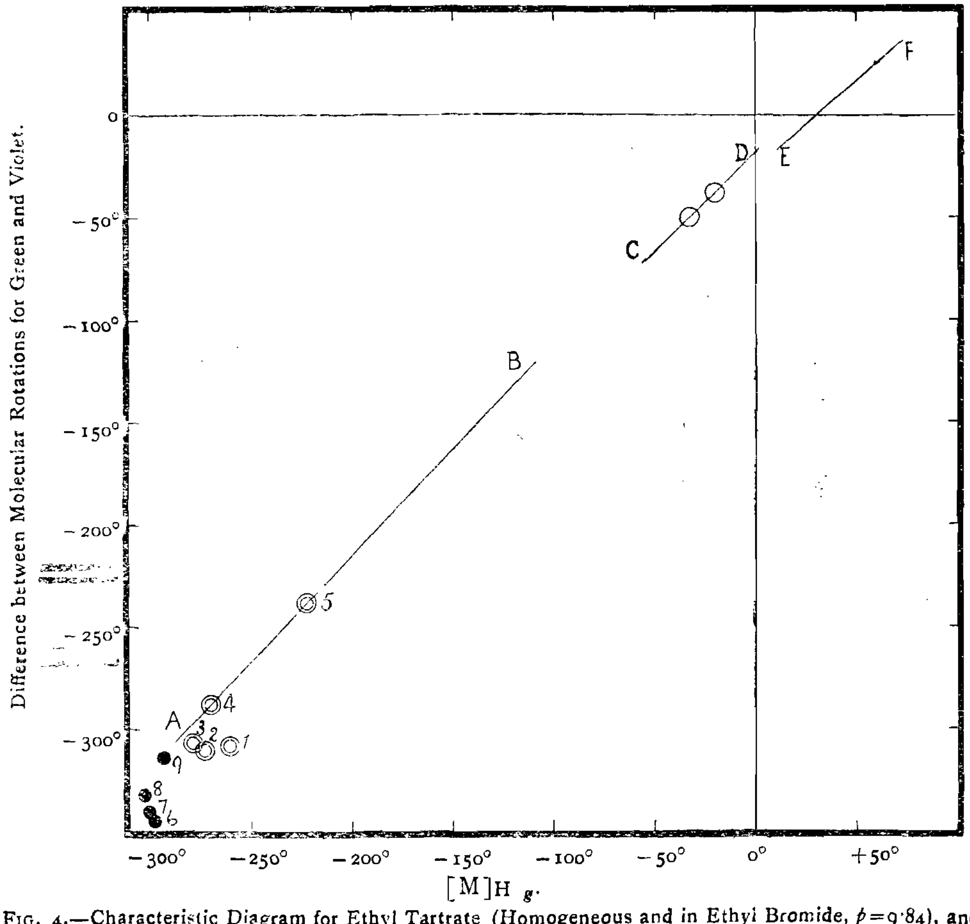


FIG. 4.—Characteristic Diagram for Ethyl Tartrate (Homogeneous and in Ethyl Bromide, $p=9.84$), and for *iso*Butyl Dibenzoyltratrate (Homogeneous and in Ethyl Bromide, $p=9.20$).

tartrate and examined its rotation over a range of temperature in the homogeneous condition as well as in solution in cinnamic aldehyde and in ethylene bromide. The results are plotted in Fig. 3, and it will be observed that the form of the curves is in agreement with the second suggestion made above. The absolute value of the rotation diminishes from red to violet; the dispersion is negative. There is a distinct minimum in each of the curves, and this minimum passes slightly towards lower temperatures as the refrangibility of the light becomes greater, although the displacement is comparatively small. The rotation tends to rise somewhat rapidly as the temperature increases; and since the appearance of the curves is not inconsistent with the possibility of intersection in the geneous ester; in ethylene bromide there appears to be some slight difference in form, which we think can hardly be due to experimental error, but to which in the meantime we can do no more than direct attention.

Since the T—R curves for homogeneous *iso*butyl tartrate and *iso*butyl dibenzoyltartrate thus show directly no common feature such as, for example, a similar maximum or minimum, or the intersection which is known as anomalous rotation-dispersion, their relationship is not so obvious as might otherwise be the case. That they are connected with one another is rendered clearer by the application of Armstrong and Walker's characteristic diagram (*Proc. Roy. Soc.*, A, 1913, lxxxviii., 392), the interpretation of which, from the point of view of the

T—R curves, has already been discussed by one of us (*Journ. Chem. Soc.*, 1916, cix., 1180, 1195). From what was there said it is to be expected that if the T—R curves for *iso*butyl dibenzoyltartrate and those for *iso*butyl tartrate or ethyl tartrate are related, as suggested above, then the experimental data corresponding to the region *y z a b c* of Fig. 1 should lie along a common line in the characteristic diagram. The points on the curve for ethyl tartrate in ethylene bromide, which clearly belong to this region, should lie along the same line, whereas points belonging to the T—R curves for *iso*butyl dibenzoyltartrate at temperatures below that at which the minimum occurs—that is to say, in the region of *x* (Fig. 1)—should not necessarily be expected to lie along the *same line* on the characteristic diagram. It will be seen from Fig. 4 that this is actually the case.

(NOTE.—The diagram is drawn according to the author's modification or Armstrong and Walker's method. Rotation values for Hg_g are plotted along the horizontal axis (the reference line), the differences between the rotation values for Hg_v and Hg_g, and Hg_y and Hg_g respectively being then plotted, according to sign, vertically above or below the corresponding values for Hg_g. The actual rotation value at any point on the diagram is the horizontal distance from the zero-point, plus (or minus) the vertical distance from the reference line.—See *Journ. Chem. Soc.*, 1916, cix., 1181).

The points marked 1, 2, and 3 (shown also in Fig. 3), for *iso*butyl dibenzoyltartrate, obviously do not lie on the line A B in Fig. 4. But the points 4 and 5, which are on the part of the curve corresponding to *z y* in Fig. 1 do lie on the line A B, and this has almost the same direction as that joining the two points for ethyl tartrate in ethylene bromide C D, both being close to that for ethyl tartrate itself, E F. Considering that we are comparing the behaviour of ethyl tartrate with that of the dibenzoyl derivative of a homologous ester, the agreement is, on the whole, very satisfactory, and it may therefore be concluded that the curves in Fig. 1 represent the influence of temperature-change upon the derivatives of tartaric acid generally; that on extending the diagram towards the left a very deep minimum is reached in the neighbourhood of low temperatures.

A slightly different way in which the connection between *iso*butyl dibenzoyltartrate and the ethyl tartrate curves might be shown is as follows:—It is reasonable to suppose that if this relationship exists, the dispersion coefficient should remain constant with varying circumstances, and should be the same for both esters. But it has been shown in a recent communication (*Journ. Chem. Soc.*, 1916, cix., 1183) that constancy can be expected only if the dispersion coefficients be calculated from what was called a rational zero. The rational zero (taking molecular rotations) for the Hg_g and Hg_v T—R curves—*i.e.*, the rotation value at their point of intersection—for homogeneous ethyl tartrate was found to be 29·4°, and when the dispersion ratio was calculated from this rotation value as zero the number 2·0989 was found (*Ibid.*, 1191). The rational zero for the green and violet lines for *iso*butyl dibenzoyltartrate cannot meantime be determined directly, but assuming the dispersion ratio to remain constant over the requisite interval, the rational zero can obviously be calculated from the rotation data at 100° and 182°, which are as follows:—

Iso*butyl Dibenzoyltartrate.*

Temperature.	100°.	182°.
$[M]_v$	−559°	−463°
$[M]_g$	−271°	−223°

Since the dispersion coefficients at these two temperatures should, by hypothesis, be the same, we must have—

$$\frac{559^\circ+x^\circ}{271^\circ+x^\circ}=\frac{463^\circ+x^\circ}{223^\circ+x^\circ},$$

where x° is the value of the rational zero. From this equation $x^\circ=17^\circ$, and setting this value in either of the above expressions, the dispersion coefficient 2·00 is obtained, very nearly the same as that of ethyl tartrate for these two colours of light. Again, taking the data for ethyl tartrate in ethylene bromide, we should have in a similar manner—

$$\frac{81^\circ+x^\circ}{32{\cdot}86^\circ+x^\circ}=\frac{58{\cdot}06^\circ+x^\circ}{20{\cdot}53^\circ+x^\circ},$$

from which $x^\circ=18{\cdot}7^\circ$, almost the same value as found for *iso*butyl dibenzoyltartrate, and, accepting this as the rational zero, the dispersion ratio is 1·96, again much the same as in homogeneous ethyl tartrate for the same two colours of light.

Organic Chemistry Department,
University of Glasgow.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 272).

Preliminary Experiments upon the Determination of Gallium, Indium, Zinc, and Aluminium in the presence of One Another.

SOLUTIONS of salts of gallium, zinc, indium, and aluminium of known concentrations were prepared as follows:—

A solution of gallium sulphate was made in the manner above described, and its concentration was ascertained by precipitation of gallium by sodium sulphite.

Indium chloride that had been prepared by Mathers (*loc. cit.*) was dissolved in water, and measured portions of this solution were boiled with a slight excess of ammonium hydroxide. The precipitated indium hydroxide was ignited to the oxide, which was then allowed to cool, was moistened with nitric acid, was reignited, and was weighed as In_2O_3.

Pure zinc sulphate was dissolved in water, and the strength of the solution was determined by precipitation with potassium mercuric thiocyanate.

The concentration of a solution of aluminium sulphate was determined by the usual method of precipitation with ammonium hydroxide.

Portions of these four solutions, carefully measured from burettes, were used to prepare the mixtures that were employed in the study of the analytical separation and determination of the four elements.

Separation and Determination of Gallium and Indium—Solutions that contained known amounts of gallium and indium were each diluted to 200 cc. A small amount of hydrochloric acid was added to each solution, and a solution of sodium hydroxide was run in until the liquid was neutral. 1·5 grms. of sodium hydroxide in excess was then added and the solution was boiled for several minutes. The resulting precipitate of indium hydroxide was collected on a filter and washed, and was then redissolved in hydrochloric acid, and the indium reprecipitated by again boiling with an excess of 1·5 grms. of sodium hydroxide. This precipitate was removed by filtration and was washed; it was then dissolved in hydrochloric acid, and the indium was determined by precipitation with ammonium hydroxide in the manner previously described. The alkaline filtrates from the two precipitations of indium were combined and were acidified with hydrochloric acid. The gallium was precipitated by sodium sulphite, the precipitate was collected on a filter and washed, was dissolved in hydrochloric acid, and the gallium

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

was reprecipitated with sodium sulphite and was finally weighed as the oxide.

TABLE VIII.—*The Separation of Gallium from Indium.*

	1.	2.	3.
Weight of Ga_2O_3 taken (grm.)..	0·0828	0·0828	0·0828
Weight of Ga_2O_3 found (grm.)..	Not det.	0·0834	0·0828
Weight of In_2O_3 taken (grm.)..	0·0647	0·0647	0·0647
Weight of In_2O_3 found (grm.)..	0·0660	0·0662	0·0676

The results for gallium are satisfactory, but those for indium are somewhat high. Later determinations of indium in the presence of gallium by this method yielded, however, very satisfactory results. (See Table XV.).

Separation and Determination of Gallium and Zinc.—Solutions containing known amounts of gallium and zinc were diluted to about 200 cc., and 2 cc. of sulphuric acid was added to each solution. The zinc was precipitated from these solutions by potassium mercuric thiocyanate. Ten cc. of hydrochloric acid was added to each filtrate, and the mercury in the filtrate was precipitated by hydrogen sulphide. After removal of the mercuric sulphide by filtration the solutions were boiled to remove hydrogen sulphide, and the gallium was precipitated by sodium sulphite. It will be seen that the results for both gallium and zinc by this method are quite satisfactory.

TABLE IX.—*The Separation of Gallium from Zinc*

	1.	2.
Weight of zinc taken (grm.) ..	0·0939	0·0939
Weight of zinc found (grm.) ..	0·0929	0·0937
Weight of Ga_2O_3 taken (grm.) ..	0·0828	0·0828
Weight of Ga_2O_3 found (grm.) ..	0·0823	0·0830

Separation and Determination of Gallium and Aluminium.—Solutions of salts of gallium and aluminium of known concentration were prepared, and the aluminium was precipitated as a hydrated chloride (Dennis, *Zeit. Anorg. Chem.*, 1895, ix., 339) by a modification of the method of Gooch ("Methods in Chemical Analysis," 1912, p. 214).

In Determination No. 1 (see Table X.) 60 cc. of hydrochloric acid was added to the solution containing gallium and aluminium, and 60 cc. of ether was then added. The flask was immersed in cold water and the liquid was saturated with hydrogen chloride. The resulting precipitate of hydrated aluminium chloride was filtered on a Gooch crucible and was washed with a mixture of 30 cc. of hydrochloric acid and 30 cc. of ether, which had been saturated with hydrogen chloride. The precipitate was then dissolved in water and the aluminium was determined by precipitation with ammonium hydroxide. A small amount of sulphuric acid was added to the filtrate from the precipitation of aluminium chloride, and the liquid was then heated until the ether and most of the hydrochloric acid had been driven off; the gallium in the solution was then thrown down by sodium sulphite.

In Determination No. 2 only 25 cc. of hydrochloric acid and 25 cc. of ether were added before the solution was saturated with hydrogen chloride. A mixture of 25 cc. of hydrochloric acid and 25 cc. of ether, saturated with hydrogen chloride, was used to wash the precipitate.

TABLE X.—*The Separation of Gallium from Aluminium.*

	1.	2.
Weight of Al_2O_3 taken (grm.) ..	0·0841	0·0841
Weight of Al_2O_3 found (grm.) ..	0·0831	0·0825
Weight of Ga_2O_3 taken (grm.) ..	0·0828	0·0083
Weight of Ga_2O_3 found (grm.) ..	0·0844	0·0098

These results were not satisfactory, but further experience with the method enabled us to obtain quite accurate analyses by this method. (See Table XVII.).

Separation and Determination of Gallium, Indium, and Zinc. First Method.—Solutions that contained known amounts of gallium, indium, and zinc, gallium preponderating, were diluted to about 100 cc. Zinc was precipitated by the addition of 25 cc. of potassium mercuric thiocyanate. After several hours' standing the precipitate was removed by filtration and the mercury in the filtrate was thrown down by hydrogen sulphide. The filtrate from this last filtration was boiled to remove hydrogen sulphide, and the indium and gallium were then separated and determined by the method previously described.

TABLE XI.—*The Separation of Gallium, Zinc, and Indium. First Method.*

	1.	2.
Weight of Ga_2O_3 taken (grm.) ..	0·0828	0·0828
Weight of Ga_2O_3 found (grm.) ..	0·0833	0·0833
Weight of zinc taken (grm.) ..	0·0038	0·0188
Weight of zinc found (grm.) ..	0·0041	0·0196
Weight of In_2O_3 taken (grm.) ..	0·0065	0·0129
Weight of In_2O_3 found (grm.) ..	0·0030	0·0075

The results for gallium were quite satisfactory, but those for zinc were high and those for indium were quite low. This may have been due to the presence of indium either in the precipitate of zinc mercuric thiocyanate, or in the precipitate of mercuric sulphide when the mercury is removed from the filtrate from the zinc precipitation. To throw light upon this point a solution that contained only indium and zinc was prepared and the zinc was precipitated as zinc mercuric thiocyanate. The excess of mercury was removed from the filtrate by hydrogen sulphide and the indium was precipitated by ammonium hydroxide.

TABLE XII.—*The Separation of Zinc and Indium.*

Weight of zinc taken (grm.) ..	0·0939
Weight of zinc found (grm.) ..	0·0969
Weight of In_2O_3 taken (grm.)..	0·0649
Weight of In_2O_3 found (grm.)..	0·0494

The result for zinc was quite high, and the precipitate of zinc mercuric thiocyanate was found to contain indium when examined before the spectroscope. This method, therefore, does not furnish a satisfactory means of determining zinc and indium in the presence of each other.

Second Method.—Solutions containing known amounts of gallium, indium, and zinc were prepared, and the indium was separated and determined by double precipitation with sodium hydroxide in the manner described previously. The alkaline filtrates from this double precipitation were combined, and the solution was neutralised with sulphuric acid. The zinc in this solution was determined by precipitation with potassium mercuric thiocyanate. The mercury in the filtrate from this precipitate was removed by hydrogen sulphide, and the gallium in the filtrate was determined by double precipitation with sodium sulphite (see *ante*).

TABLE XIII.—*The Separation of Gallium, Zinc, and Indium. Second Method.*

No.	Wt. of Ga_2O_3 taken. Grm.	Wt. of Ga_2O_3 found. Grm.	Wt. of zinc taken. Grm.	Wt. of zinc found. Grm.	Wt. of In_2O_3 taken. Grm.	Wt. of In_2O_3 found. Grm.
1.	0·0828	0·0813	0·0186	0·0171	0·0130	0·0129
2.	0·0828	0·0827	0·0367	0·0337	0·0323	0·0318
3.	0·0828	0·0821	0·0939	0·0926	0·0647	0·0650
4.	0·0828	0·0817	0·0075	0·0049	0·0065	0·0063
5.	0·0083	0·0079	0·0939	0·0944	0·0323	0·0335
6.	0·0828	Not det.	0·0188	0·0161	0·0130	0·0120
7.	0·0083	0·0061	0·0939	0·0942	0·0194	0·0195
8.	0·0083	0·0085	0·0075	0·0050	0·0647	0·0680

In Determinations 3, 5, and 7 an excess of 3 grms. of sodium hydroxide instead of the usual amount of 1·5 grms. was employed for the first precipitation of indium hydroxide. In Determinations Nos. 1 and 2 the precipitated indium hydroxide was dissolved in hydrochloric acid. In the other determinations it was dissolved in sulphuric acid.

It was found that in some cases zinc was present in the filtrate from the final precipitation of indium by ammonium hydroxide. Consequently, in all of the determinations except Nos. 1 and 2 this filtrate was treated with potassium mercuric thiocyanate, and any precipitate that formed was added to the main precipitate of zinc mercuric thiocyanate. An examination of the table will show that the results for gallium and indium were quite satisfactory in nearly every case, but that those for zinc were inaccurate, especially when the amount of zinc was small.

Third Method.—Solutions containing known amounts of gallium, indium, and zinc were diluted to about 200 cc., and 2 cc. of sulphuric acid (sp. gr. 1·84) was added to each solution. Zinc was precipitated as zinc mercuric thiocyanate in the usual manner. After standing for several hours this precipitate was collected on an asbestos filter in an unweighed Gooch crucible, and was washed with a solution containing 20 cc. of potassium mercuric thiocyanate reagent in 1 litre. The precipitate was then treated on the asbestos mat in the crucible alternately with a few drops of a strong solution of sodium hydroxide and a few drops of concentrated hydrochloric acid until it was dissolved. Four cc. of acid was sufficient to effect solution of the precipitate. The resulting solution was then diluted to about 200 cc., and the excess of acid was neutralised with sodium hydroxide. Two cc. of concentrated sulphuric acid and 20 cc. of the potassium mercuric thiocyanate reagent were then added. The contents of the beaker were allowed to stand for several hours, and the precipitate was collected in a weighed Gooch crucible which was then dried and weighed.

The combined filtrates from the two precipitations of zinc mercuric thiocyanate had a volume of about 500 cc. Ten cc. of hydrochloric acid was added to the solution, the mercury was precipitated by hydrogen sulphide, the mercuric sulphide was filtered off, and the filtrate was freed from hydrogen sulphide by boiling. The indium and gallium in the solution were determined by the method previously described.

Table XIV.—*Separation of Gallium, Zinc, and Indium. Third Method.*

	1.	2.	3.
Weight of Ga_2O_3 taken (grm.) ..	0·0828	0·0166	0·0083
Weight of Ga_2O_3 found (grm.) ..	0·0840	0·0163	0·0094
Weight of zinc taken (grm.) ..	0·0076	0·0188	0·0939
Weight of zinc found (grm.) ..	0·0077	0·0188	0·0939
Weight of In_2O_3 taken (grm.) .	0·0064	0·0647	0·0130
Weight of In_2O_3 found (grm.) ..	0·0014	0·0502	0·0039

It will be seen that the results for zinc were very satisfactory and that those for gallium were fairly accurate. The amount of indium, however, was low in each case, and it was found that the precipitate of mercuric sulphide gave a strong spectrum of indium.

(To be continued).

Wolfram.—One of the noteworthy consequences of the war, according to *Metall und Erz*, is the great increase in the output of wolfram. Before the war the whole world-production did not exceed 10,000 tons annually. The present output is at least double that quantity. An approximate estimate gives—Portugal, Spain, France, and Great Britain, 2500 to 2800 tons; North America, 6000 tons; South America, 3000 to 3500 tons; India, Siam, the Malay States, and Australia, 5500 to 6000 tons; China and Japan, with Indo-China, 800 to 1200 tons. The stimulus has been high prices, so that a drop in market value would close some of the mines. Russia certainly possesses deposits of wolfram. South America, Spain, and some other countries favourable to Germany may be expected to ship to her wolfram ore at prices considerably below the present abnormally high level.—*Royal Society of Arts.*

A SPECIFIC GRAVITY APPARATUS FOR GASES.*

By EDWARD J. BRADY.

The simplest method of determining the specific gravity of gas would be by means of a U-tube with liquid in the lower end, similar to the method used for determining the density of liquids. This method has not been used for gases, because of the extremely small differential pressure that would have to be measured to obtain accuracy. The pressure gauge in the preceding note makes the use of this method possible.

The apparatus devised consisted of a tall tube, through which the gas was passed, having its lower end connected with the precision gauge by means of a four-way cock. At the upper end there is a pilot flame, if the gases being measured are inflammable. The gases being measured passed through this vertical tube, which is opened to the air through a suitable burner at the top. A quarter turn of the cock cuts off the gas and connects this column of gas with the precision pressure gauge, which will immediately indicate a slight suction produced on the gauge, provided that the gas is lighter than the air. This cock may be turned a number of times to obtain check readings on the same sample of gas. Using the telescope and scale as described, we may graduate the scale to read in specific gravity direct. The gravity as shown by a tube of this kind would, of course, include any foreign matter, such as particles of dust or vapours. But, inasmuch as these materials assist in producing the differential pressure in the Pitot tube or the Venturi meter, they should be taken into consideration in applying the formula for these instruments.

Gases heavier than air, such as oxygen, carbon dioxide, &c., may also be measured, the deflection produced being in the opposite direction.

For more accurate work, where the absolute density of the gas is wanted, we might provide a vertical tube for air also. This air could be dried to eliminate the effect of moisture and the whole system surrounded by the constant temperature bath.

Where the density of hot gases relative to air are required, the vertical air pipe could be carried *within* the vertical gas pipe, so that the air would quickly assume the same temperature as the gas being measured. In many places a vertical tube of much greater height would be permissible. In this case the telescope and scale could be dispensed with and the differential pressure read from the Vernier direct.—*Journal of the Franklin Institute*, clxxxvii., No. 4.

BOROUGH POLYTECHNIC INSTITUTE.

The following Report was read at the Twenty-sixth Annual Distribution of Prizes and Certificates by Principal C. T. Millis, M.I.Mech.E., on Tuesday, May 27, 1919:—

The year ending July, 1918, the fourth year of the great war, was a memorable and trying one, but in spite of that the Institute kept up its many activities and did much good work, including war service. Of course in number of students, especially of men, we have suffered, but have probably been more fortunate than some other institutes. There were 2094 students and members in attendance during the year, 1550 being evening and 540 full time day students.

As regards examination successes, out of the 325 papers worked by evening students 209 qualified for passes. One Silver Medal and £1, being first prize in Millinery awarded by the City and Guilds of London Institute, was won by Lily K. Rowe, who was also awarded the Chairman's Prize of £3 for the best record during three consecutive

* Note from the Physical Laboratory of the United Gas Improvement Company, U.S.A.

years, being the first woman student to gain this prize. Four Medallions for First Aid and fourteen L.C.C. Evening Exhibitions in Science and Technology were gained. The boys of the Day School gained 43 diplomas and certificates on the results of a final examination and their three years of good work.

The Board of Education having given up its examinations, the Governors have drawn up a scheme of Institute Examinations, and students under definite conditions will be able to obtain diplomas for successes at examinations in organised courses of study extending over three years. The scheme is an important one, requiring care and thought. We believe the diplomas will be recognised outside the Institute as being of real value as evidence of sound work on the part of the students. A careful perusal of the examination lists in your hands will show that many students by their successes in two or more subjects during their first and second years are on the way towards gaining the Institute Diplomas to which I have referred, and, indeed, some students have qualified for the Diplomas. Diplomas and Certificates will be ready shortly.

I repeat what I have said on former occasions. Much work done by pupils of the Institute is not shown by examination results; for example, the Girls' Trade School at present has no certificate examination scheme. The real test of our work lies not in examination results but in the progress of our students. We have ample evidence in their successful careers that their studies have been of real value to them as citizens and workers. This has been shown during the war.

The staffing of the Institute during the past two or three years has been very difficult, and we have been fortunate in having the services of three mistresses who have done good work for our Boys' School. Much extra work and responsibility have been thrown on the permanent teaching staff and officials, who have willingly responded. I must pay a well deserved tribute to the zeal and energy of those Heads of Departments and the Staff generally who have so loyally helped me to carry on. Many appointments have now to be made to replace the temporary staff. Dr. Henderson, Head of the Electrotechnics Department, who has been on service for some time, has resigned, having been appointed Staff Officer for the Army Education Scheme.

I am sure you will all hear with regret that our Lady Superintendent is retiring in July next. Miss Smith, Mr. Richardson, and I were appointed in 1892 to start the work of the Institute (Mr. Richardson retired in 1915). Miss Smith and I have worked together for twenty-seven years, and naturally I shall miss her very much. It is not an easy matter to do justice to her work. All who have worked with her here know the splendid work she has done. She is the pioneer of the Girls' Trade School movement, and no one will be able to give more energy, thought, and devoted service to the Institute than she has given. I am sure that the staff, members, and students will desire to join with me in wishing her many years of health and happiness in her retirement.

I now pass to the consideration of the future work of the Institute. We feel that next session there will be a considerable increase in the number of students, which will tax the accommodation to its utmost. There is some doubt at present as to the effect of the new Education Act on our work in the future. Young persons of fourteen to sixteen years of age will doubtless receive education of a more or less general character and will be accommodated in special buildings. The compulsory part time education for those between sixteen and eighteen will not come into operation for seven years, and in that work this Institute may be expected to take a prominent part so far as science and technical work is concerned in both day and evening classes. Our Branch Institute, Herold's Institute, Bermondsey, will probably at first be utilised in the day time for the pupils of fourteen to sixteen years of age. One effect of the compulsory part-time day continuation education will be an increase in the number of girls and boys seeking admission into junior technical schools, because the new Education Act grants exemption from attendance at part-time day courses to those children who have attended full-time day classes up to sixteen years of age, and this will act as an incentive to thoughtful parents to keep their children at such schools until that age. Moreover, employers will be more likely to engage workers at sixteen years of age who are exempt from attending school than to engage those at fourteen years of age who will be compelled to attend eight hours a week in the day time until they are eighteen.

Then, again, it will be necessary to consider how our evening education will be affected by this Act. If the part-time day education is properly planned and directed it should stimulate the pupils to further efforts and provide us with a large number of students able to go on with higher work than at present. The work of the Mechanical Engineering, Electrotechnics, Chemistry, and other departments of the Institute will have to be extended in the future, and probably the methods of instruction, particularly in the laboratories and workshops, may require modification to meet changing and specialised methods of production. The compulsory part-time day education will doubtless exert an influence on our evening work outside that of science and technology. Owing to the co-ordination of education in London, our work is becoming more technical, and therefore we must pay increased attention to the study of subjects of general interest, such as music, literature, modern languages, social and industrial economics, industrial history, to enable our students to broaden their training and make intelligent use of the extra leisure which we hope they will have in the future. I am aware that this is not an easy task, and I appeal to the members and students to give all the assistance they can to help in the development of this side of our work, so that the Governors may be able to provide facilities for them to become not only good workers but good citizens for this great country of ours.

Now the war is over and peace is in sight I may briefly review the war services rendered by the Institute.

We know of over 850 students and members who voluntarily joined the Army. The *Polytechnic News* has been sent each month to members on service. This was done at the suggestion of Mr. Edric Bayley, who largely defrayed the cost of postage and printing. Letters have been received from all parts of the world and published in the *News*. Service members and students have expressed their appreciation of the Institute's efforts to keep in touch with them.

I regret to say that of these over 100 have made the great sacrifice. They will not be forgotten, and their names will be recorded on the War Memorial which it is hoped to place in the Institute. Many distinctions have been gained and a number of commissions have been obtained.

Early in the war our Farriery Institute in Bermondsey proved of the greatest service to the Army in training at a critical time over 1500 men belonging to the Royal Field Artillery, the Royal Engineers, and Army Service Corps in cold shoeing. The Institute was also lent for the reception, inspection, and dispatch of horse-shoes required for the Army. I do not think the value of this work has been sufficiently appreciated.

Instruction was given in the Polytechnic at the beginning of the war in telephony, wheelwrights' work, and saddlery to 100 men of the Royal Field and Royal Horse Artillery. A member of the Chemistry staff was given a commission in the Sanitary Section, and over thirty men of the R.A.M.C. were trained in water analysis. Our Chemistry staff took an active part, with other Polytechnics, in the preparation of drugs for local anæsthetics not previously made in this country, and also rendered services in utilisation of waste products, for which letters of thanks have been received.

From July, 1915, until the Armistice was signed our

engineers' workshop with the staff was given up to munitions work, and over 10,000 inspection and other high-class gauges so necessary for munitions work were manufactured, and successfully passed the tests of the National Physical Laboratory. A really fine record of work.

The Southwark Volunteer Corps was started in the Institute, with Major Basil Williams, a member of the Governing Body, as its Commandant. The Institute gymnasium, rifle range, and the athletic ground were lent, and proved of great service to men of the New Army as well as to the volunteer corps.

The Southwark Voluntary Aid Detachment was started by our members, with Miss Swayne as Commandant, and has done excellent work in hospitals. From the commencement of air raids until the end of the war the Institute was used as a dressing station and as a refuge, members of the V.A.D. being in attendance every night, and they and the working staff deserve great praise for their devotion to duty. A presentation of watches, medals, and certificates was made by the Governors at the re-union on Empire Day.

The members, evening students, girls and boys of the day schools have collected very nearly £400 for soldiers' comforts and other funds. The girls and women students and members have also worked a large number of articles for soldiers and for the Red Cross Society.

Considerable attention has been paid to the training of disabled soldiers to enable them to become dental mechanics and motor mechanics, over 150 having been in training. Advice and assistance has also been given to help forward the Army Education Scheme, and a large number of Army and Ex-Army men have received technical training.

The large hall and men's gymnasium were lent for the manufacture and Government inspection of anti-gas masks; from 15,000 to 18,000 being sent out every day.

I think I have said enough in this brief survey to give you some idea of the service which the Institute has rendered in connection with the war, and I believe you will agree with me that it forms a record of which we have every reason to be proud.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY CONVERSAZIONE.

THE first Soirée since 1914 took place on May 28. The gathering was quite on the old lines, and many familiar faces were seen in the rooms at Burlington House. The absence too of many was noted, for during the past four years many prominent men of science have passed away.

The meeting was very well attended, and although there was nothing particularly striking in the exhibits there were many of considerable interest, showing that even during the war there has been found opportunity for research in other fields than those devoted to annihilation.

Among the more important exhibits were the following:—

Prof. ERNEST WILSON. Instruments for measuring Minute Susceptibilities, including a Portable Instrument for Survey Work.

The action of the instrument depends upon the mechanical force exerted by a magnetic field on a magnetic material placed in it, the force per unit volume bing proportional to the gradient of the square of the field. It is ultimately measured by a galvanometric method involving the action of a spot of light, except in the case of the portable instrument, when a pointer is more convenient.

Prof. H. F. NEWALL, F.R.S. Dr. G. E. Hale's photographs of the Zeeman Effect in the Spectra of Sunspots.

An image of the sun's disc is thrown by means of the 150 ft. tower telescope at Mount Wilson on the slit plate of the 75 ft. spectrograph. Close to the slit a Nicol prism is placed. Above the Nicol prism are mounted strips of mica 2 mm. wide with their axes inclined $+45^{\circ}$ and -45° to the length of the strips, alternating in adjacent strips. This device is called a compound quarter-wave plate.

When a sunspot near the centre of the sun's disc falls on the slit through the polariscopic apparatus, certain lines in the spectrum are widened, others are resolved into two or three components.

From a comparison of the solar effects and of the magnitude of the Zeeman effect in experiments in the laboratory on the corresponding lines, the strength of the magnetic field in the sunspot is deduced.

Average spots exhibit fields ranging from 2000 to 2700 gausses. The field varies approximately in proportion to the size of the umbra.

Mr. A. MALLOCK, F.R.S. Apparatus used in the measurement of the Growth of Trees.

An "Invar" tape was passed round the tree and over the "Rockers" on the apparatus whose arms control the angle between a plane glass surface and the face of a right-angled glass prism. The growth of the tree continually alters this angle, the variation of which was measured by observing the change of position of the interference bands formed, at grazing incidence, between the plane and prism. The details of the procedure are given in *Proc. R.S.*, 1918, xc., B., p. 186 *et seq.*

Dr. J. S. HALDANE, F.R.S. Army form of apparatus for continuous Oxygen administration.

In cases of poisoning by irritant gas, and in various other conditions, one of the main dangers is due to the fact that the partial pressure of oxygen in the lungs becomes inadequate to oxygenate the blood. It is therefore necessary to add oxygen to the inspired air until a sufficient degree of recovery takes place. With the help of a reducing valve and graduated tap, a constant stream of oxygen of the required amount is delivered into the small bag attached to the face-piece. This bag is emptied at each inspiration, none of the oxygen being wasted. The administration can thus be continued, if necessary, for several days, as the consumption of oxygen is reduced to a minimum.

The DIRECTOR OF RESEARCH, AIR MINISTRY. Liquid Oxygen Container (50 lbs. capacity), and Liquid Oxygen Vaporiser Flask (5 litre).

These vessels comprise an inner and outer metal shell, the intervening space being evacuated. Charcoal is placed in the vacuum.

Sir WILLIAM GARFORTH. Photographs, &c., illustrating Pressure in Explosions.

1. Photograph of coal-dust flame, 170 feet long, being expelled from experimental tube, with particulars of registered velocities and preseures.

2. Photograph showing a shale-dust cloud being expelled from an experimental tube by an explosion of coal-dust, the flame of which was extinguished within the tube by its contact with incombustible dust.

3. Plan showing the destructive effects of a coal-dust explosion on mine workings, and how the explosion flame was extinguished on coming in contact with incombustible shale-dust.

Prof. MACGREGOR-MORRIS. Portable Apparatus for measuring Air Currents.

A Wheatstone bridge is made of four wires all exactly alike of a material whose resistivity varies with temperature. This bridge is heated by the passage of an electric current. Adjacent arms are so arranged as to be unequally cooled when placed in an air current. The apparatus can be carried on a bicycle, and has been used for determining the velocity of the wind about a cliff edge, and also around the gallery of a lighthouse.

Sir NAPIER SHAW, F.R.S. Illustrations of the Structure of the Atmosphere on selected occasions.

1. Records of wind, on tube-anemometers, corrected for the difference of exposure in different orientations.

2. Maps of stream-function of the air for different levels on the occasion of the destruction of a fleet of Zeppelins, October 19-20, 1917, and another similar distribution on October 13, 1918.

3. Theoretical maps of the stream-function of the free air and distribution of pressure in the case of a cyclone consisting of a simple vortex with maximum velocity 43 metres per second, enclosing a core of fluid-rotating-like-a-solid, in a uniform atmospheric current of 16 metres per second; with maps for 18h., September 10, 1903, for comparison.

Dr. G. SIMS WOODHEAD and Dr. VARRIER JONES. Quasi-continuous temperature recording apparatus for clinical use, and specimens of records obtained.

The outfit consists of a resistance thermometer with compensating leads, a galvanometer with "bridge" and resistances, by means of which a wide range of temperature changes may be observed, and a Cambridge thread recorder, which gives a quasi-continuous (at half-minute intervals) and permanent record of the temperature of the human or animal body. This apparatus has been of use in determining the diurnal variations of temperature of normal subjects and in studying febrile conditions in disease, *i.e.*, tuberculosis. Continuous temperature records for seventy-two hours are readily obtained.

THE CAMBRIDGE SCIENTIFIC INSTRUMENT CO., LTD. Dr. G. A. Shakespear's Katharometer for Measuring the Purity of Gases.

Two small spirals of platinum wire form two arms of a Wheatstone bridge, and their resistances, depending on their temperatures, depend on the viscosities of the surrounding gases. A galvanometer connected across the bridge indicates its out of balance and is calibrated to give a direct reading of the purity of the gas, or otherwise as required. Many practical applications are possible: (*a*) A Hydrogen purity meter for use with aircraft is exhibited; (*b*) Permeameters for testing airship fabrics and exploring seams or searching for leaks are exhibited; (*c*) a humidity recorder showing the vapour pressure in the air of the exhibition room was shown working.

Mr. F. W. ASTON. Rapidly moving Striated Discharge in Neon and Helium.

The light in the capillary of a spectrum discharge tube containing neon or helium is apparently continuous, but when analysed by a rotating mirror is found to consist of a procession of alternate bright and dark bands or striations travelling in the direction of the current, *i.e.*, from anode to cathode. These appear in the mirror as ribbons of light, their waviness indicating variations in speed and being more marked in neon than in helium. The mean velocity can be calculated from the slope, and is found to be approximately that of pressure wave propagation, *i.e.*, sound, in the gas in the discharge tube.

Mr. C. T. R. WILSON, F.R.S. 1. Stereoscopic Photographs of the Tracks of Ionising Particles through Air.

By causing water to condense upon the ions set free, the invisible trail of ions left by each flying particle along its course is converted into a sharp defined line of cloud. Stereoscopic photographs of the tracks thus rendered visible are taken before convection currents have had time to distort them.

The photographs exhibited illustrate the nature of ionisation by the alpha and beta rays from radium and by X-rays.

2. Photographic record of the changes in the Electric Potential Gradient during a Thunderstorm.

The record was obtained at the Solar Physics Observatory, Cambridge, on June 13, 1917. It shows the sudden changes produced in the electric field by the passage of lightning discharges.

Mr. A. CHASTON CHAPMAN. "Mineral Yeast"—Used in Germany during the War for Human Food.

The organism exhibited is very similar to, if not identical with, the so-called "Mineral Yeast" which was manufactured in Germany in considerable quantities during the War and used to supplement the bread ration. The organism is not a true yeast—that is to say, it does not belong to the genus *Saccharomyces*. It grows freely upon nutrient solutions at a temperature of 38° to 40° C., forming a thick greasy crinkled film. It does not produce alcohol, and the time needed for a full crop is about thirty-six to forty-eight hours. The separated organism contains 50 to 55 per cent of protein (NX6·25) and about 5 per cent of fat, expressed on the moisture-free material. It is entirely free from bitterness, and has a pleasant flavour, suggestive of that of cream cheese. As a source of carbon, glucose or molasses answer well, and the organism is capable of supplying the whole of its nitrogen needs from ammonium salts—that is to say, it does not require any organic nitrogen. In addition to the above, phosphates must be present and small quantities of potassium and magnesium salts. The conversion products of sawdust forms a good pabulum for the organism, and can be used to replace glucose and molasses.

Mr. GEORGE H. GABB. Portrait of Dr. John Jeffries, in pastel, by John Russel, R.A. Dr. Jeffries was, with Blanchard, the first to cross the Channel in a Balloon, on January 7, 1785.

The account of this epoch-making "aerial voyage" was read before the Royal Society in January, 1786. This portrait was exhibited in the Royal Academy in 1786, and was lost for over 100 years until it was discovered a short time ago, quite unknown, among a miscellaneous collection of pictures. Dr. Jeffries, although famous as being the first aeronaut to cross the Channel, his title to a niche in the Temple of Science is perhaps yet more secure to immortality as being indisputably the first to make an ascent solely for scientific purposes, and the first to attempt meteorological observations from a balloon. In his ascent from London on November 30, 1784, he included in his scientific equipment a barometer, a thermometer, a hygrometer, an electrometer, a marine compass, a telescope, and six small phials filled with water given him by Cavendish in order to collect samples of air at different altitudes. This last experiment was made at the suggestion of Dr. Blagden, Secretary to the Royal Society.

Sir ROBERT HADFIELD, F.R.S. Stereoscopic Radiographs of large Carbon Electrodes.

These electrodes are used in electric steel smelting furnaces, the largest type being no less than 22 inches in diameter. For effective and economical working of the furnaces it is essential that the electrodes do not break and fall into the bath. The finer the structure of the electrode and the fewer the inclusions, the less does the possibility of breakage arise. The stereoscope shows four different types of electrodes which are largely used.

War Research on Nitrogen Fixation.

For the past three years the Research Laboratory of the Munitions Inventions Department, constituted under the auspices of the Nitrogen Products Committee of the Ministry of Munitions, has been conducting experimental investigations on various methods for the fixation of nitrogen. The most important divisions of the work have been concerned with the Synthesis of Ammonia, the Oxidation of Ammonia and Preparation of Nitrates, and the Preparation and Purification of Hydrogen. Experiments illustrative of the work of three of the sections were shown as follows:—

1. Synthetic Ammonia Section.—Apparatus for the study of Catalysts.

An example of the small apparatus used in the study of the effect of velocity, temperature, pressure, purity of gases, &c., on the behaviour of catalysts at pressures up to 200 atm. is shown at work. In order to be able to carry out rapid tests of catalytic-efficiency the dimensions are intentionally made small. Specimens representative of

several hundred preparations of catalytic materials are shown.

2. Nitrates Section.—A new process for the direct production of Solid Ammonium Nitrate.

The process depends upon the interaction of ammonia with air taking place in three stages :—

(a) The oxidation of ammonia by atmospheric oxygen to nitric oxide;

(b) The further oxidation of nitric oxide ;

(c) The direct formation of ammonium nitrate from ammonia, water vapour, and oxides of nitrogen.

It had long been considered impossible to prepare ammonium nitrate free from nitrite by direct synthesis. When the different constituents are mixed in anything like molecular proportions very poor yields containing much nitrite are obtained. The results of the investigation have shown that by proper control of the experimental conditions a solid dry product free from nitrite can be obtained by a comparatively simple process. This form of ammonium nitrate differs from the ordinary crystalline material and possesses a number of interesting properties.

3. Hydrogen Section.

Seeing that three-quarters of the cost of synthetic ammonia consists in the preparation and purification of the high grade hydrogen required, a very important branch of the work has been the study of modern catalytic methods for its production at a low cost and a thorough investigation of the different methods for its purification. New catalytic processes dependent on fractional combustion have been devised and some of these have proved successful on an industrial scale. Two new developments are shown in operation :—

(i.) A recorder for indicating automatically the percentage of carbon monoxide in a flow of hydrogen.

(ii.) A process for the removal of H_2S as sulphur by fractional catalytic combustion.

Charts, diagrams, and apparatus illustrative of the Laboratory work were also exhibited.

Demonstrations were given by Major G. W. C. Kaye on the Detection of Defects in Aeroplane Timber, and by Dr. R. T. Leiper on Biological Factors in the Spread and Control of Bilharziasis.

SOCIETY OF GLASS TECHNOLOGY.

The May meeting was held on Wednesday, the 21st ult., in the Institute of Chemistry, Russell Square, London.

Dr. M. W. Travers, F.R.S., presided over a well attended meeting.

After the usual formal business had been transacted, Dr. Walter Rosenhain, F.R.S, gave a most interesting and instructive lecture on "*Some Phenomena of Pot Attack.*" The lecture was an account of work on entirely new lines, carried out under Dr. Rosenhain's supervision by Mr. E. A. Coad-Pryor, B.A., Mr. V. Stott, M.Sc., and Miss A. B. Taylor.

In the first place the lecturer stated that research was begun on the improvement of methods for the production of optical glass. The first step was to find a material to arrest the attack of molten glass, and to endeavour if possible to discover a container entirely insoluble in glass at high temperatures. A study of glass attack upon clay was begun, and the process by which glass attacks clay investigated. These processes, owing to the novel methods used, could be carefully controlled under standardised conditions. Small pots made of china clay cast by a special method was used in the research. The furnace used was an electrical one, so constructed that temperature and atmosphere could be kept constant. The pot attack of several glasses known to be very violent in their action upon clay was studied. The amount of pot attack was measured exactly under various time and temperature conditions. The result showed that the attack was mainly on the bottom of the pot, and that holes were drilled in a rough circular form. In many cases it was shown that the amount of attack was proportional to the depth of the clay beneath the glass surface. The explanation of the results was somewhat difficult to find, but a study of solution of solids in liquids less viscous than glass led to the conclusion that the phenomenon was due to currents set up in the liquid due to density changes. By means of a lantern the lecturer showed the processes of solution actually taking place. One of the portions of the research had been the microscopic examination of the glass and pot after attack. Much interesting information had been obtained, and slides were shown illustrating some of the results. This portion of the work is necessarily still in progress. It had been proved conclusively that holes could be drilled in a pot without having actual defects in the pot to start with. Another very interesting feature recently developed was the application of X-rays to the examination of small pots. In concluding his lecture, Dr. Rosenhain pointed out the fundamental importance of being able to do quantitative work upon the actual melting processes of glass.

In the discussion that followed, Dr. Travers, F.R.S., Mr. C. J. Peddle, M.Sc., F.I.C., Mr. E. A. Coad-Pryor, B.A., Mr. Duncan Webb, jun., and Mr. Arnold Stevenson, B.A., M.B.E., took part.

During the morning the Society paid a visit to the National Physical Laboratory at the invitation of the Director, Sir Richard Glazebrook, F.R.S., and a most interesting morning was spent in inspecting the following departments :—Engineering and Aerodynamics, Electrotechnics, Optics, Metrology, Tank, Metallurgy and Glass Research.

The best thanks of the Society are due to Sir Richard Glazebrook and Dr. Rosenhain for their splendid reception, and also to the staff of the National Physical Laboratory, who contributed so much to the pleasure of the visitors.

The next meeting of the Society will be held at Sheffield on June 18.

NOTES.

The demand for radium for both therapeutic and physical work is steadily increasing; there is now no doubt about its value in the treatment of rodent ulcer and many forms of skin diseases. During the war it has been extensively employed for the preparation of luminous paints for the dials of instruments used in night operations on land, in the sea, and in the air; all these applications are likely to be permanent. Although the actual amount of radium in luminous paint is small—about 0·25 mgrm. of radium element to the grm. of zinc sulphide—the high price of radium compounds makes this a matter of serious consideration. A radio element having similar properties, *i.e.*, *mesothorium*, is comparatively plentiful, being obtained almost as a by-product in the preparation of thoria, used in the "mantle" industry. This is now rapidly coming into use; it, however, has the defect that its "life" (the period in which its initial activity is reduced to half value) is only from five to six years, as compared with 1600 years for pure radium. At the present moment there appears to be no ready way of distinguishing the one compound from the other. In a great many of its applications a life of six years is quite sufficient, but, on the other hand, where it is used for medical and some other purposes, the matter becomes very serious. It is to be hoped that some means may be found for clearly distinguishing between the two compounds.

Farmers and Fertilisers.—At the close of the present month the *control* exercised for the last two years by the Board of Agriculture over the prices of fertilisers to farmers comes to an end. What that *control* has meant to farmers in the supplying of fertilisers at considerably

less than prime cost may be gathered from a statement by Lord Ernle, President of the Board of Agriculture, in the House of Lords on Wednesday, May 7, when he stated that "the assistance given to the farmer with his fertilisers has cost the State something like £1,600,000 last year." The manufacture of superphosphate and compound manures (only one section of the fertilisers referred to by Lord Ernle) has been controlled during these last two years by the Ministry of Munitions, which supplied the manufacturers with the raw materials on a basis which permitted the sale of superphosphate and compound manures at the pricee fixed by the Food Production Section of the Board of Agriculture, these being such as to encourage a liberal use of artificial manures by farmers in the interests of the maximum possible food production within these Islands. Now that the *control* of the fertiliser industry, with others, is being abandoned and the manufacturers have to supply themselves with their raw material at the market prices and independently of Government aid, it must naturally follow that the prices of manufactured fertilisers must be based upon the cost of raw materials. The farmers of the country must, therefore, anticipate after the close of the present month a substantial increase in the price of superphosphate and compound manures, which will continue until such time as the present high overseas freights return to a more or less normal level.

Caution as to Worthless Manures.—A correspondent has forwarded a circular sent out by a certain firm—not one of the recognised manure manufacturers—offering as fertiliser a material described as a complete mineral plant food at the price of £10 per ton. Analysis showed that the material contained no nitrogen, no phosphate, and only a small amount of potash; there was, however, a little calcium carbonate, but the bulk was inert mineral matter. Farmers and allotment holders cannot be cautioned too strongly agained specious advertisements claiming unusual powers for particular proprietary articles. A large number of experiments have been made by fully qualified and disinterested persons in many parts of the country and with many crops and substances, and no authentic record exists to show that any substances are of use as fertiliser to farmers in this country except compounds of nitrogen, phosphorus, potassium, certain compounds of calcium (*i.e.*, lime, limestone, and gypsum), and sodium (salt and sodium sulphate). Most of these substances are worth buying. A few experiments indicate that magnesium compounds may, under certain circumstances, be of some use, though not very much; in Italy manganese compounds have been supposed to be of value, though British experiments have not supported this view; while iron compounds have also been considered as fertilisers. Neither magnesium, iron, nor manganese compounds, however, are worth paying for, as their action is far too uncertain to justify expenditure by any except the most adventurous of experimentally-minded growers. As to other substances there is still less indication that they ever possess value. Before paying for any fertiliser farmers should demand the proper invoice and should see that they are really obtaining full value for their money.—*Journal of the Board of Agriculture*, May, 1919.

The Federation of British Industries are organising a British Manufacturers Exhibition in Athens, to be held in October and November next, and at the present moment there is a great demand in Greece for practically every description of manufactured article produced in this country. The fact will probably be appreciated that the Exhibition affords an exceptional opportunity of introducing goods to Greek buyers in advance of manufacturers of other nationalities. There is still some space available in the Exhibition, but early application is advisable from manufacturers. The articles mentioned by the Federation's Special Commissioner in Athens as being greatly in demand are as follows:—Machinery of every description, particularly agricultural machinery; Railway rolling stock, &c.; Cotton goods and clothing of every description; Boots and shoes; Electric dynamos, &c.; Automatic telephones; Fertilisers and chemicals generally; Food products; Toilet requisites, soaps, &c.; Household requisites of every description; Jewellery; Stationery; Furniture (both Household and Office); &c.

British Chemical Standards (Chrome-Vanadium Steel "V").—In response to a special appeal to prepare alloy steel standard turnings of the above type, a supply has been obtained and analysed by three Government Departments, a number of independent analysts, steel manufacturers, and motor or aero makers' chemists, thus representing in the main the different sections of the industries concerned. The analysis is as follows:—

Carbon	0·574	per cent
Silicon	0·158	"
Sulphur	0·063	"
Phosphorus	0·024	"
Manganese	0·543	"
Arsenic	0·015	"
Chromium	0·858	"
Vanadium	0·271	"

The turnings are now available at a price just sufficient to cover the cost and are packed in 50 and 100 grm. lots, with each of which is issued the usual certificate giving details of the analysis. Further particulars may be obtained from Headquarters, 3, Wilson Street, Middlesbrough.

Attention is directed to the new Government publication *Surplus*, the official organ of the Surplus Government Property Disposal Board, Ministry of Munitions, which will be published on the 1st and 15th of every month. The first number just issued is a thoroughly businesslike production. It enumerates the great variety of surplus war material that is for disposal all over the country, and is so classified that manufacturers and traders are able to get in touch at once with the materials they wish to secure. A long list of chemicals for disposal is given, in quantities varying from a few pounds to tons. Among the "miscellaneous stores" the following chemical apparatus appears: — Fortins Barometer (in case). Chemical Balances Oertling, Nos. 21, 32a, 7.S.B., 8.S.B.2. Platinum crucibles, foil, basins, and rods. Thermometers, Gas Meters. Iron stands for Lunges. Gas volumeters. Hydrometers, Geryk Vacuum Pump Duplex C. Electric Motors, 110 V.A.C. Clamps, Fletcher's Aspirators, Gutta Percha Nitrometer, also a large quantity of glass and other Laboratory fittings. (Lying at Oldbury. Reference D.B.5.C.). Also Large Glass Aspirators, Amp and Volt Meter and Resistance coil. Calorimeter by Alex. Wright—for fuel testing with thermometer, Electric control, Ether thalpelassimeter Steam oven, fitted with still. Portable pyrometer (by Scientific Co., Cambridge), High temperature (boiler) Thermometers, 4 and 5 ft. steel sheaths. Wash bottle, capacity 1 litre. Water purification apparatus (incomplete). A large quantity of Hydrometers, also glass and other laboratory appliances. (Lying at Victoria Works, Northwich. Reference D.B.5.C., Caxton House, Westminster, S.W. 1)." Applications for copies of *Surplus* are being received in large numbers by the Ministry, but it should be known that orders for its delivery can be placed with newsagents. The price is 3d. for each number.

MEETINGS FOR THE WEEK

Monday, June 16.

Royal Geographical, 8.30. "Tibesti to Darfur," by Lieut.-Col. J. Tilho.

Thursday, June 19.

Institution of Mining Engineers, 11 a.m. (Dinner at Waldorf Hotel, 7).

Friday, June 20.

Institution of Mining Engineers. (Visit to Docks and Warehouses of Port of London Authority).

THE CHEMICAL NEWS

VOL. CXVIII., No. 3088.

A SYSTEM OF STRUCTURE SYMBOLS.

By INGO W. D. HACKH.

THE idea underlying a system of structure symbols for organic compounds was first published about a year ago (*Canadian Chem. Journ.*, 1918, ii., 135). Although the principle remained unaltered its form has passed since that time through various stages of development (*Science*, N.S., 1918, xlviii., 333), making it possible to present it now in a more perfected form.

The system is based upon an extremely simple principle which does not involve any new conception but merely provides an efficient, compact, and accurate device for the representation of certain facts of organic chemistry. It is well known that certain information regarding organic

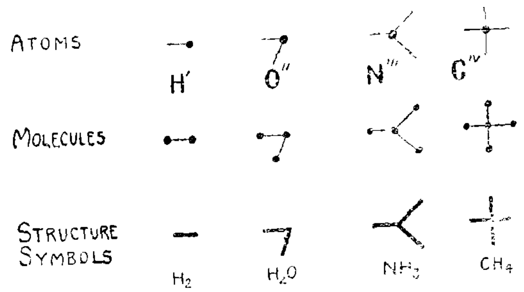


FIG. 1.

compounds is conveyed in a progressive series of (*a*) empirical, (*b*) rational, and (*c*) structural formula, the last type being the most advanced form. Unfortunately the space occupied by structural formulæ restrict their use mainly to didactic purposes in the illustration of isomerism and stereo-isomerism. The system of structure symbols enable a more extensive use of the information contained in structure formula, at the same time preserving clearness and accuracy and limiting the space, thus the ambiguity inherent to the rational formula is avoided.

Assuming a definite valency of H = 1, O = 2, N = 3 or 5, and C = 4 as being the normal condition of these four

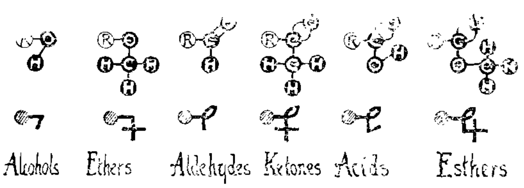


FIG. 2.

elements in organic compounds, Fig. 1 shows the key to the system.

In this figure the atoms are represented by points from which one, two, three, or four lines respectively radiate. In the molecule these lines representing the bonds are connected, and in the structure symbols the points standing for the four types of atoms are determined by the lines thus—

Where *one* line begins or ends—HYDROGEN,
Where *two* lines radiate (angle)—OXYGEN,
Where *three* (or *five*) lines radiate—NITRATE,
Where *four* lines radiate (two lines cross)—CARBON.

Thus the simplest structure symbols are the ones shown for hydrogen gas, water, ammonia, and methane.

In order to avoid confusion in the structure symbols of the more complex compounds it is well to become familiar with the appearance of the different radicals and groups. Thus the symbols for the six important types of organic compounds show in each case a distinct and characteristic form. This Fig. 2 illustrates also the relationship between alcohols and ethers (methyl-ethers), aldehydes and

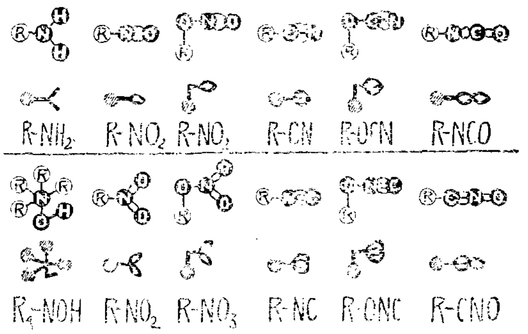


FIG. 3.

ketones, acids and esters, in each case the H being replaced by the CH_3 group. The H which is being replaced by the organic radical R is indicated in the symbols by a shaded circle. Fig. 3 gives the symbols for a number of organic nitrogen compounds, illustrating schematically the relationship of tri- and penta-valent N.

With the help of the above principle the structure symbols of Figs. 4 and 5 will be readily deciphered. In

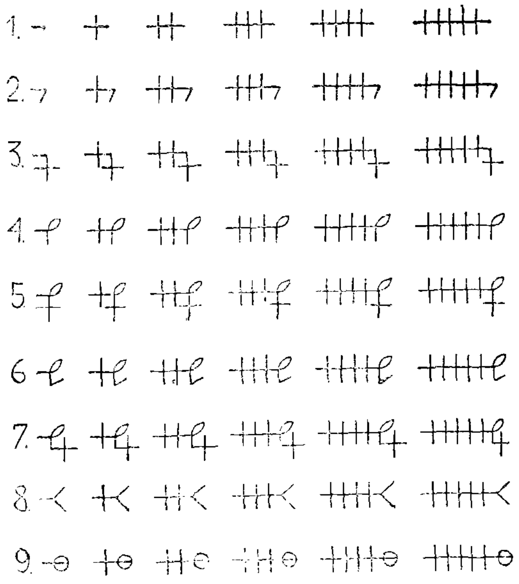


FIG. 4.

the first row are the hydrocarbons, row 2 shows the alcohols, row 3 the methyl-ethers, row 4 the aldehydes, row 5 the methyl ketones, row 6 the acids, row 7 the methyl esters, row 8 the mono-amines, row 9 the cyanides. It is interesting to note that in this systematic schema CH_3OH and CH_3COH is listed twice, namely as alcohol and aldehyde, and also as "hydrogen-methyl-ether" and "hydrogen-methyl-ketone." The benzene derivatives and the illustration of the ortho-, meta-, and para-compounds need no comment.

In the practical experience gained in teaching organic chemistry by this method it has become advisable to formulate a few rules—

Aliphatic chains containing more than six carbon atoms

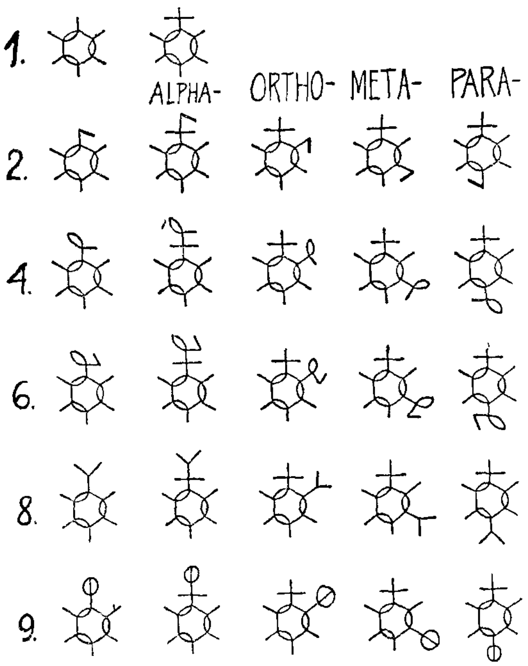


Fig. 5.

are written alternately short and long, the fifth line being longer in order to enable an easier count.

Asymmetric carbon atoms are indicated by a dot (Fig. 6) at the junction of the two lines; the rotatory power of the compound is indicated by the direction of the tail of the

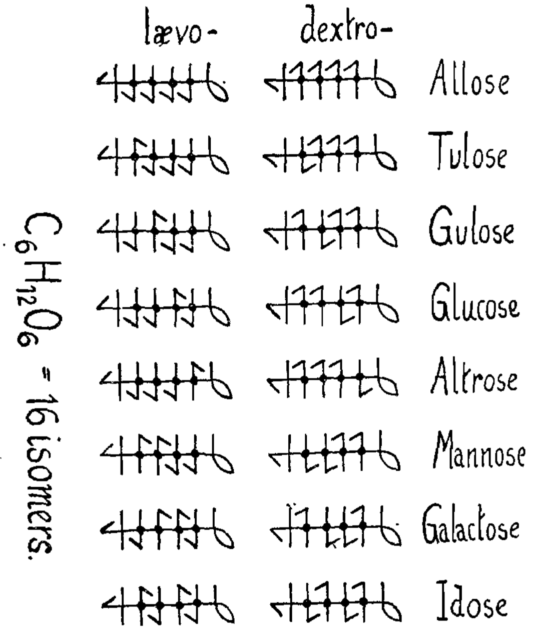


Fig. 6.

—C—OH group; in levo-compounds this points in the direction of the clock-hand movement, in dextro-compounds in the reverse direction, in inactive compounds the direction of the different tails will balance each other, in racemic compounds the dot indicating asymmetric carbon atoms is eliminated.

All other elements entering into an organic compound are represented by their respective "inorganic" symbol, *e.g.*, Cl, I, Br, S, Fe, &c.

Heterocyclic rings are better characterised by indicating the heterocyclic atom (N or O) by a dot outside the ring. The nitrogen-hydrogen line is preferably written toward the centre of the ring, thus attention is drawn to the point of interest.

In Fig. 6 the sixteen isomeric hexoses are given, and it is noteworthy that the information contained in such a narrow compass would have required at least a full printed page if the customary writing of structure formulæ had been employed.

As has been pointed out in the preliminary papers the advantages of the system are numerous, for they save space and time and are valuable in the class-room. Their simple principle is without exception readily understood by the student and force him to write a theoretically correct structure, otherwise not all the given atoms would be represented. This leads to accuracy and a definite placing of eventual double or triple bonds. The accuracy and compactness of the symbols should make them also of value in abstracting and in hand-books where ordinarily the structure formula of an organic compound is omitted. The writer hopes that the system may become of service to the chemical world and will be glad to accept constructive criticism.

College of Physicians and Surgeons,
San Francisco, April 19, 1919.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Continued from p. 283).

The Separation and Determination of Gallium, Indium, Zinc, and Aluminium.—Solutions that contained known amounts of gallium, indium, zinc, and aluminium were treated essentially as previously outlined, up to the first precipitation of gallium by sodium sulphite. In this precipitation the hydroxides of both gallium and aluminium were precipitated by sodium sulphite, and this mixture of hydroxides was then dissolved in hydrochloric acid, and the gallium and aluminium were separated by the method described previously.

TABLE XV.—*The Separation of Gallium, Zinc, Indium, and Aluminium.*

	1.	2.	3.
Weight of Ga_2O_3 taken (grm.)..	0·0828	0·1056	0·0414
Weight of Ga_2O_3 found (grm.)..	0·0797	0·1052	0·0429
Weight of In_2O_3 taken (grm.) .	0·0323	0·0323	0·0647
Weight of In_2O_3 found (grm.) ..	0·032[illegible]	0·0328	0·0655
Weight of zinc taken (grm.) ..	0·0376	0·0376	0·0939
Weight of zinc found (grm.) ..	0·0363	0·0381	0·0939
Weight of Al_2O_3 taken (grm.) ..	0·0841	0·0841	0·0280
Weight of Al_2O_3 found (grm.) ..	0·0852	0·0840	0·0273

The results given in Table XV. show that the determination of each of the four elements was fairly satisfactory in all of the three analyses.

These preliminary experimants upon the analytical

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J. Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

separation of gallium, indium, zinc, and aluminium indicated that the most accurate results would be obtained by the determination of zinc and gallium in one sample and of indium and gallium in a second sample, the aluminium being determined in either of the two samples.

Further investigation in this direction led to the adoption of the procedure described below.

Method of Analysis of Mixtures containing Gallium, Indium, Zinc, and Aluminium.

Neutral or slightly acid solutions of two samples of the material to be analysed are prepared. Sample 1, in which zinc and gallium (and aluminium) are to be determined, should not contain more than 0·1 grm. of zinc. Sample 2, in which indium and gallium (and aluminium) are to be determined, should not contain more than 0·1 grm. of indium. The accurate determination of zinc is made in Sample 1; that of indium in Sample 2. Gallium and aluminium may be determined in whichever of the two samples these elements are present in amounts most suitable for analysis.

Determination of Zinc and Gallium (and Aluminium) in Sample 1.—The neutral or slightly acid solution of the sample is diluted to 200 cc. and 2 cc. of concentrated sulphuric acid is added. The reagent solution of potassium mercuric thiocyanate (see *ante*) is then added drop by drop to the solution, which is vigorously stirred throughout the addition. After the precipitate has begun to form 20 cc. more of the precipitant is added, and the solution is allowed to stand for several hours with occasional stirring. The precipitate is then collected in an unweighed Gooch crucible, and is washed with a solution that is prepared by diluting 20 cc. of potassium mercuric thiocyanate reagent to 1 litre. A few drops of a concentrated solution of sodium hydroxide and then a few drops of concentrated hydrochloric acid are alternately poured upon the precipitate, and between successive additions of these reagents small quantities of water are run through the crucible. The precipitate should be entirely dissolved by the use of not more than 4 cc. of hydrochloric acid. If this solution of the zinc precipitate is acid it is neutralised with sodium hydroxide; if it is alkaline it is neutralised with sulphuric acid. It is then diluted to 200 cc., 2 cc. of concentrated sulphuric acid is added, and the zinc is precipitated with 20 cc. of the potassium mercuric thiocyanate reagent in the manner above described. After several hours' standing the precipitate is filtered through a weighed Gooch crucible, and is washed with the dilute solution of potassium mercuric thiocyanate above mentioned. The precipitate is then dried in the crucible at 105—110° and is weighed. The zinc factor is 0·1314.

If it is desired to determine gallium, or gallium and aluminium, in this sample the filtrates from the two precipitations of zinc are combined, 5 cc. of concentrated hydrochloric acid is added to the solution, and the mercury is precipitated by hydrogen sulphide. The precipitate of mercuric sulphide is filtered off and washed. The filtrate is boiled to expel hydrogen sulphide and is then neutralised with sodium hydroxide. 1·5 grms. of sodium hydroxide dissolved in a little water is then added to the solution, which is next boiled for several minutes. The resulting indium hydroxide is collected on a filter-paper and is washed with hot water, and the filtrate is set aside. The precipitate of indium hydroxide is then redissolved in hydrochloric acid, the solution is diluted to 100 cc., 1·5 grms. of sodium hydroxide is added, and the solution is again boiled to reprecipitate indium as the hydroxide. This precipitate is collected on a filter and is washed with hot water; the filtrate from this precipitation is then combined with the filtrate from the first precipitation. 1·5 grms. of hydrated sodium sulphite, $Na_2SO_3.7H_2O$, is dissolved in a little water and is added to the solution. Hydrochloric acid is next run in, a drop at a time, until the solution is distinctly acid to litmus paper. The liquid is then boiled for about six minutes. The resulting precipitate consists of gallium hydroxide together with aluminium hydroxide if aluminium is also present. It is collected on a filter-paper and is washed with a little hot water. To make sure that the precipitation of gallium has been complete a small amount of sodium sulphite is added to the filtrate and the solution is boiled for several minutes. If no precipitate results the solution is made slightly acid with acetic acid and is boiled for a further twenty minutes. Any additional precipitate from either of these treatments is added to the precipitated hydroxide first obtained.

If no aluminium is present the gallium hydroxide is dissolved in hydrochloric acid and the solution is diluted to 200 cc. The solution is then made slightly alkaline with ammonium hydroxide, and 1·5 grms. of hydrated sodium sulphite is then added. The solution is then made slightly acid with hydrochloric acid and is boiled for about six minutes. The resulting precipitate of gallium hydroxide is collected on an ashless filter-paper and is washed with water until free from chlorides. The filtrate should be tested as above described to ascertain whether the precipitation of gallium has been complete. The gallium hydroxide is dried on the paper and is incinerated over the Bunsen flame and weighed as Ga_2O_3.

If aluminium is present the precipitate of the hydroxides of gallium and aluminium is dissolved in not more than 25 cc of concentrated hydrochloric acid. An equal volume of ether is added to this solution. The flask is immersed in cold water and the solution is saturated with hydrogen chloride. The precipitated hydrated aluminium chloride is collected on an unweighed Gooch filter. The precipitate is washed with a small amount of a cold mixture of equal volumes of concentrated hydrochloric acid and ether, this mixture having first been saturated with hydrogen chloride. The precipitate is then dissolved in water, and the aluminium is determined by precipitation with ammonium hydroxide in the usual manner. The filtrate from the aluminium chloride precipitate contains the gallium. One cc. of sulphuric acid is added to this solution, which is then boiled until most of the ether and hydrochloric acid have been expelled. The solution is then diluted to 200 cc., and the gallium is determined by precipitation with sodium sulphite in the manner above described.

Determination of Indium and Gallium (and Aluminium) in Sample 2.—Sample 2, in which indium is to be determined, is diluted to 100 cc., and 1·5 grms. of sodium hydroxide in excess of the amount of this substance required to neutralise the solution is added. The liquid is then boiled for several minutes, and the resulting precipitate of indium hydroxide is collected on a filter-paper, is washed with hot water, and is then dissolved in hydrochloric acid. This solution is neutralised with sodium hydroxide as before, 1·5 grms. of sodium hydroxide is then added, and the solution is boiled for several minutes. This second precipitate of indium hydroxide is dissolved in hydrochloric acid, ammonium hydroxide is added until the solution is slightly alkaline, and the liquid is boiled for several minutes. The precipitated indium hydroxide is collected on an ashless filter-paper, is washed with hot water, and is then dried. It is next ignited in a weighed crucible over a Bunsen flame, the crucible is allowed to cool, the oxide is moistened with a few drops of nitric acid, is heated carefully to remove the excess of nitric acid, and is then again highly heated over a Bunsen flame and is weighed as In_2O_3.

The alkaline filtrates from the two precipitations of indium by sodium hydroxide contain the gallium and aluminium that may have been present in the sample. To determine these two elements the solution is neutralised with sulphuric acid, and then 1 cc. of concentrated sulphuric acid is added for every 100 cc. of the solution. Zinc is precipitated from this acid solution by the addition of from 30 to 40 cc. of the potassium mercuric thiocyanate reagent. The contents of the beaker are allowed to stand for several hours, and the precipitate is then collected on a filter and is washed with a solution containing 20 cc

of the potassium mercuric thiocyanate reagent to the litre. Five cc. of hydrochloric acid is added to the filtrate, and mercury is then precipitated by hydrogen sulphide, the mercuric sulphide is removed by filtration and is washed, and the filtrate is then freed from hydrogen sulphide by boiling. Gallium and aluminium may then be determined in this solution by the method described under "Sample 1."

The oxides of gallium, indium, and aluminium are somewhat hygroscopic. For this reason the crucible that contains the ignited oxide should in each case be weighed in a stoppered weighing bottle.

Results that were obtained in analyses of mixtures containing gallium, indium, zinc, and aluminium by the use of the methods just described are given in Tables XVI. and XVII.

TABLE XVI. *Determination of Zinc and Gallium in Sample 1.*

	1.	2.	3.
Zinc taken (grm.) ..	0·0076	0·0188	0·0939
Zinc found (grm.) ..	0·0077	0·0188	0·0939
Ga_2O_3 taken (grm.) ..	0·0828	0·0166	0·0083
Ga_2O_3 found (grm.) ..	0·0840	0·0163	0·0094
In_2O_3 present (grm.) ..	0·0064	0·0647	0·0130

TABLE XVII.—*Determination of Indium, Gallium (and Aluminium) in Sample 2.*

No.	In_2O_3 taken. Grm.	In_2O_3 found. Grm.	Ga_2O_3 taken. Grm.	Ga_2O_3 found. Grm.	Al_2O_3 taken. Grm.	Al_2O_3 found. Grm.	Zinc present. Grm.
1.	0·0323	0·0328	0·1056	0·1052	0·0841	0·0840	0·0376
2.	0·0647	0·0655	0·0414	0·0429	0·0280	0·0273	0·0939
3.	0·0323	0·0320	0·0828	0·0797	0·0841	0·0852	0·0376
4.	0·0130	0·0129	0·0828	0·0813	None	—	0·0188
5.	0·0323	0·0318	0·0828	0·0827	None	—	0·0367
6.	0·0647	0·0650	0·0828	0·0821	None	—	0·0939
7.	0·0065	0·0063	0·0828	0·0817	None	—	0·0075
8.	0·0323	0·0335	0·0083	0·0079	None	—	0·0939
9.	0·0194	0·0195	0·0083	0·0061	None	—	0·0939
10.	0·0647	0·0680	0·0083	0·0085	None	—	0·0075

(To be continued).

THE NATURE OF THE LIQUID SURFACE.*

By H. R. PROCTOR, D.Sc.

MOST scientific people have noticed the curious persistence of errors which, once they have crept into text-books, are copied from one to another without question. The experienced hand notes them and passes on, being generally too busy to correct the legion of text-books even if he reads them, but to the student they are often a source of much perplexity and misunderstanding. It is this consideration which induces me to discuss a statement which has appeared in recent books on colloid chemistry, and has even formed the basis of elaborate theories of the colloid state, but which I believe to be entirely without basis in fact. It is, to quote from a recent work, "that the surface is under greater pressure than the bulk of the liquid owing to the contracting force of surface tension"—"a conclusion which has many important corollaries"—and, of course if the conclusion is unsound the corollaries fall with it. The error seems to have arisen from assuming that surface tension was the cause instead of the effect of internal pressure, and so "putting the cart before the horse."

I fear that to make the case clear to chemists who are not physicists I must deal with some rather elementary matters, for which I apologise to those to whom they are already familiar. The internal pressure of liquids is simply the result of the mutual attraction of their molecules, which holds them together and prevents them from flying off into vapour, and is analogous to (if not identical with) the cohesion of solids. In liquids, however, the molecules, being further apart, and equally attracted from all sides, can move freely *within* the liquid surface, though to liberate them *from* it, the large amount of energy known as the "heat of evaporation" must be expended. It may seem curious at first sight that these attractions, enormous as they can be shown to be at molecular distances, are so little obvious to ordinary observation, but it must be realised that they are intra-molecular and confined within the liquid surface, and, that to be truly within the liquid in a molecular sense, a body must be actually dissolved in it. The attractions diminish very rapidly with distance, so that they are only really effective over spaces which must probably be measured in hundred-millionths of a mm. Thus they are generally negligible in gases unless strongly compressed, when they diminish elasticity, and even bring about liquefaction. In Van der Waals' well-known gas-equation, $(p + \frac{a}{v^2})(v - b) = RT$, the term $\frac{a}{v^2}$ represents these attractions or internal pressure, which thus behaves as a direct addition to the external pressure, while b is a correction for the actual volume of the molecules which cannot be compressed. When these corrections are taken into account with suitable constants the gas equation holds very approximately even for liquids.

So far it has proved impossible to measure the internal pressure directly, though qualitatively it can be proved to exist. It has been shown that quite large forces are required to break the continuity of a gas-free liquid sealed in a glass tube so that no free surface exists, and the well known "bumping" or successive boiling of gas-free liquids is due to the difficulty of steam forming a new surface in the interior of the liquid. Indirectly, it has been shown by Stefan that in bringing a molecule into the actual surface half the work is accomplished which is required to set it free in the form of vapour, and, since the total "heat of evaporation" is known, the internal pressure overcome in bringing a molecule to the surface is easily calculated, and it proves to be enormous. For ether at its boiling-point the calculated pressure is 1284, and for water at 0° C. 11,000 atm., or about 72 tons per sq. inch.

If we imagine Stefan's molecule on the surface (that is, half in and half out) we shall see that it is attracted downwards and to all sides by the other molecules within the very small hemisphere of its molecular range of attractions, but as there are no molecules above it there is nothing to attract it upwards or counterbalance these downward attractions, while the molecules around and below it pull it at all angles of obliquity below the horizontal. By a device well known to mathematicians each of these oblique forces can be "resolved into" or represented by two smaller forces, one vertical and the other horizontal, and all these attractions of the hemisphere finally resolved into one force pulling vertically downwards, and two equal and opposed forces pulling horizontally in any two opposite directions, and these horizontal forces are what constitute surface tension, a force tending to draw together and contract the surface in every direction. On water, which has a higher tension than any other common liquid, the force amounts to about 75 dynes (say, mgrms.) across the linear centimetre.

From what has been said it will be seen that the surface tension is not a new force in itself, but merely a resolved part of the internal pressure, and in extending the surface we diminish its internal pressure to the same amount as the surface energy has been increased, or, in other words, lessen, not increase its compression. If we follow Stefan's conception so far as to suppose the surface extended to one molecule in thickness the whole of the internal pressure will have disappeared, and as there are two surfaces the whole of the work will have been done which is necessary

* From the *Journal of the Society of Leather Trades' Chemists*, iii., No. 4. (Communicated by the Author).

to convert the liquid into vapour, and there is no longer any vertical component to prevent its passing into the gaseous state.

Both the internal pressure and the surface tension diminish with the rise of temperature from the opposing effect of the heat energy. If σ_0 be the surface tension at some known temperature, and σ_t that at another, $\sigma t = \sigma_0(1 - \gamma t)$, γ being a small constant, usually about 0·003, and the temperature being in C°. Plotted on curve paper this gives a straight line, sloping down from t_0 to t if t be the higher of the two. Obviously there is a temperature at which this line must cross the zero line, and this point proves to be very approximately the "critical" temperature at which the liquid and its vapour become equal in density, and as there is no longer any distinction between them both surface and surface tension disappear. It is probable that even at ordinary temperatures the actual liquid surface, far from being a region of compression is a sort of critical layer, where a film of expanded liquid merges into one of compressed vapour, for the molecular attraction cannot cease suddenly at the liquid surface, but must attract the vapour molecules above it. This, in fact, almost follows from the theory of vapour pressure, which is the equilibrium of pressure at which as many vapour molecules fall into the liquid surface and are caught by it as escape from it in the form of vapour. Van der Waals gives a differential equation connecting the surface tension with the rate of fall of density in the surface layer. There is probably no break in the curve of density in passing through the surface, but only a very rapid change of direction. In the gas-equation the term $\frac{a}{v^2}$ expressing the internal pressure appears as a simple addition to the mechanical pressure of the gas.

Thermodynamic considerations prove that the extension of surface is accompanied by loss of heat; that is to say, that the heat energy of the liquid has been consumed in overcoming the attraction of the molecules, just as heat is consumed when a liquid evaporates. It is therefore a fair conclusion that the formation of surface is accompanied by expansion and not by contraction.

It seems a mechanical misconception to suppose that pressure applied to the surface of a liquid the particles of which are free to move in any direction could produce a local compression on the surface, since the pressure must be equally distributed throughout the liquid as if it were confined in a stretched rubber skin, to which surface tension has often been compared. Local compression could only be produced by attractive forces directed towards the region of pressure. *Ex hypothesi*, surface tension is a *tension* and not a pressure, and though it produces a pressure within a convex surface it must stretch and expand the surface layer itself. Such a pressure is easily observed in a drop hanging to a pipette, which recedes when the pressure is relieved by sloping the pipette, and where the radius of curvature is short, as in a very small drop, it may become very considerable. The equation to such a pressure is $p = \frac{2\sigma}{\gamma}$, where σ is the surface tension and γ the radius, and the pressure increases inversely as the radius. In a globule of water in air of 0·001 mm. in radius γ would be about 15 atm. Where the surface is flat no pressure is produced, and the liquid under concave surfaces is in tension, as is seen by the rise of liquids in capillary tubes.

There is one sense, however, in which the surface may be said to be under greater pressure (though not greater compression) than the bulk of the liquid. In the surface the unbalanced downward component of the attractions tends to draw a particle downward and inward with a maximum force, while within this force is balanced by others drawing in an opposite sense, so that the particle is equally free to move in every direction. A mass on the earth's surface has a maximum *weight* or downward pressure, but is exposed to no external pressure but that of the atmosphere. If it were moved to the centre of the earth it would have *no* weight, but be exposed to the enormous compression of the superincumbent mass. Possibly the analogy is a closer one than appears at first sight; for we need not suppose that the attraction of gravitation vanishes at molecular distances, though it is probably modified by other forces, and there is some reason to believe that it varies inversely as the fourth power of the distance like that of a small magnet (Lewis, "A System of Physical Chemistry," I., p. 11, Longmans, 1916), and the differences between the attraction which governs the solar system and that which causes internal pressure may well arise from the fact that the one is exerted by enormous masses over hundreds of millions of miles, and the other by almost infinitesimal particles over hundred-millionths of a mm.! The thickness of the surface film has been estimated as of the order of the last named quantity (10^{-8} cm.), and if so, two particles within it must attract each other with ten thousand million million (10^{+16}) times the force they would exert on each other at 1 cm. apart, so that gravitation alone may well account for enormous attractions at molecular distances.

The facts which have been adduced are, I think, sufficient to disprove the theory of a compressed surface, but there are several other points which it is interesting to notice. I do not propose to discuss the effect of electric potential on surface tension in detail, since, important as it is to the chemist, it would open too many side issues for this paper. Since charged particles, where + or − repel others of the same sign, a charged surface tends to spread in opposition to surface tension, which, if the charge is sufficient, may even become negative. On this depends the action of the capillary electrometer which is sensitive to charges so small as 0·001 volt. The most important cases are those of charged interfaces between two liquids which are charged with opposite signs. Such charges continually arise from the accumulation of positive or negative ions on the surfaces, and probably play a leading part in the stability of emulsions and colloid solutions generally, and on their precipitation by electrolytes.

So far our attention has been practically confined to what may be called "free" liquid surfaces in contact only with their own vapour, or with an inert gas of which the influence may be generally neglected, though in some cases the gas or vapour may be so condensed on the surface by its attraction as to appreciably influence the tension. A class of surfaces, however, which are still more important in chemistry and colloid theory are those which form the interface between a liquid and a solid, or between two immiscible liquids; and here again assertions have been made and assumptions tacitly accepted which do not seem in harmony with known facts.

If one liquid be poured upon another with which it is not miscible, in a test-tube, an interface is formed between them which is much flatter than that on either of the individual liquids in air, and may be concave or convex towards the upper liquid; that is to say, the surface tension is smaller towards another liquid than to air or vapour. The cause is obvious—the whole of the attractive forces are no longer resolved on the surface as to their horizontal components, but a portion of the attractive forces of each passes through the surface and is exerted on the neighbouring liquid. It seems to be experimentally proved that, between liquids at least, the remaining common tension of the interface is equal to the difference between the two single ones if it is taken into account that in many if not in all cases some mutual solution takes place which usually lowers surface tension, and that the individual tensions to be considered are not those of the pure liquids but of the saturated solutions of either in the other. If this rule is really exact it is obviously impossible to find three liquids A, B, and C, of which the tensions A − B + B − C are less than the tension A − C, and in no such case has ever been observed, though it has been stated that it is possible when one of the series is a solid,

and a theory of the action of protective colloids has been built on the supposition.

It appears, therefore, that with liquids at least the common tension of the interface results from the unaltered individual tensions of the two liquids acting in opposite directions, and it follows that while the positive value of the greater tension is reduced, that of the less becomes a minus quantity, and it tends, not to contract, but to spread on the surface of contact; while it is a matter of observation that many liquids, like oil on water, do not apparently spread but form lenticular drops on the surface. The explanation appears to be that when a drop of oil is placed on clean water it immediately spreads and covers the latter with a thin and invisible film, and if the surface were infinite would do so without limit. When, however, a surface becomes covered with a film of oil of a thickness approaching the range of molecular attraction its surface tension is reduced till it becomes less than that of the oil itself, which consequently ceases to spread and forms a drop. When a liquid refuses to spread on a surface of higher tension, it is because the latter is already covered with a film of grease or some other impurity which reduces its surface tension below that of the other. It has been shown that clean water will spread spontaneously on a surface of clean mercury, and of course the same reasoning applies to solid surfaces. As all surfaces attract not merely liquids but gas and vapours it is possible that in some cases the interfering film may be one of compressed gas, or of condensed vapour.

If in a system of two liquids, that with the lower tension tends to spread upon the other, this must be still more the case when of three substances the tension of one is lower than that of either of the others, since on both sides of its film the tension becomes minus, and it spreads in a thin layer between them. If the system is one of a solid (of which the surface tension, or at least the internal pressure is always high), and of an emulsion-colloid, the surface must become coated with whichever of the colloid constituents has the lowest tension, and the "adsorption" will closely obey the so-called adsorption-law, the exponent depending on the fall of attraction with the thickening of the absorbed film (see Note). It is not improbable that such a coating may explain the action of protective colloids on suspensoid sols.

The bearing of these facts on the formation of emulsions is obvious. If two immiscible liquids are shaken together the one present in less quantity becomes mixed with the other in the form of small globules bounded by an interface of the enclosed and enclosing liquids, and whichever of the two has the highest will retain a positive surface tension, while that of the other will become negative and tend to spread, the common interface tension as a whole remaining always positive. It is obvious that the nearer the two are to equality and the less will be this common tension, and the less the tendency of the separate globules to coalesce under its influence, and if the tensions of the two became actually equal all tendency to coalesce into separate liquids would disappear, and actual solution or a permanent colloidal sol would be formed, and any slight disturbing cause, such as a difference of potential, would cause this to take place spontaneously. The more common case of permanent emulsion, however, is that in which three constituents take part. If a little soap, or alkali which forms soap with the free fatty acid be added, it lowers the surface tension of both the other constituents, and probably forms an intermediate layer between them, so that there is no longer any tendency for globules to coalesce. Many colloids when they accumulate on a surface have a tendency to undergo some condensation which is irreversible, and enables them to form an insoluble skin, and this would render the emulsion still more permanent.

It would be interesting to consider the bearing of the facts which have been stated on the Willard Gibbs theory of mechanical adsorption, which, in my opinion, has been called in to explain many actions to which it does not apply; but any full discussion would exceed the necessary limits of this paper. The theory is based on thermodynamic considerations, and is usually stated in the form of a differential equation not very comprehensible to others than mathematicians, so that it may be worth while to explain its reasoning in other than mathematical language. If a substance of lower surface tension is dissolved in a liquid it lowers the surface tension of the latter, and Gibbs shows that such a substance tends to accumulate in the surface, and still further to lower the tension, and with it the surface energy (which is the surface tension × the surface) which tends to reduce itself in every possible way. At the same time the concentration of the substance in the surface creates an opposing osmotic pressure in the surface layer, and equilibrium is reached when the loss of surface energy is equal to the gain in osmotic. Thus, other things being equal, the more the substance reduces surface tension, and the larger its molecule (and consequently the less the osmotic pressure it exerts) and the greater will be its accumulation in the surface, and both these conditions specially apply to some of the organic substances which most lower surface tension.

The thermodynamic reasoning on which the proof depends neither attempts nor requires any explanation of the manner in which a substance lowers surface tension, or of the force which draws it to the surface; but it may be suggested that such substances are necessarily those of which the attraction for the molecules of the solvent is low, and which consequently are expelled from a region of higher to one of lower internal pressure.

It has so far proved impossible quantitatively to test Gibbs's equation, but it has been shown by Zawidski and others (*Zeit. Phys. Chem.*, 1900, xxxv., 77) that froth contains more of the tension-lowering substance than the bulk of the liquid, and that globules of air rising through a liquid carry with them a concentrated layer in their ascent (Benson, *Am. Journ. Phys. Chem.*, 1903, vii., 532; Milner, *Phil. Mag.*, 1907, [VI], xiii., 96).

The conclusion may therefore be regarded as proved so far as free liquid surfaces are concerned, but when we have to deal with interfaces where the tension of one of the substances is negative and the surface density is increased and not diminished, it is hard to see how the Gibbs phenomenon can occur. Nevertheless it has been freely used by advocates of adsorption theories, without a word of comment or defence, to explain adsorptions from liquids by solid bodies such as charcoal.

Note.

The adsorption formula is $\frac{x}{m} = a\,c^{\frac{1}{n}}$, where x is the weight of substance adsorbed; m that of the adsorbing substance; c the volume-concentration of the solution after adsorption; a and n constants. As the adsorbing substance is porous or finely-divided, and therefore of large but indeterminate surface, x is a proportionate measure of the surface employed, and $\frac{x}{m}$ with some multiplying constant represents the weight or thickness of the adsorbed layer. a presumably represents this multiplying constant, and, theoretically, should depend on the surface of the adsorbent and not on the nature of the adsorbed body. The exponent $1/n$ represents the rate of diminution of the adsorbing attraction as the film thickens or the attraction becomes saturated. If the adsorption is a real reversible equilibrium there must for any given thickness of film be a definite solution-pressure corresponding to the concentration of the solution. This solution-pressure will increase as the film gets thicker from the lessened attraction of the adsorbent, or the greater saturation of its attraction. The formula is wholly empirical, and probably never accurately represents the actual adsorption-law, as the logs. of experimental adsorption-curves rarely if ever give exactly straight lines, but have usually a quite definite curvature.

MEASUREMENT OF THE THICKNESS OF FILM FORMED ON GLASS AND SAND.*

By EARL PETTIJOHN.

Introduction.

A large amount of work has been done up to the present time on the formation of a film on the surface of glass or silica, in which water has been used as the liquid to produce the film. Thus Ihmori (*Wied. Ann.*, 1887, xxxi., 1006), Parks (*Phil. Mag.*, 1903 [6], v., 517), Briggs (*Journ. Phys. Chem.*, 1905, ix., 617), Katz (*Proc. Acad. Wetenschappen*, 1915, p. 445), and Langmuir (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 2221) give values for the thickness of the film formed on glass, silicate, or quartz surfaces.

There is a considerable difference in the values obtained as might be expected, since the materials used differed considerably in chemical composition and nature of surface. A part of the material was in the form of small grains (sand and quartz), some being relatively coarse and some extremely fine powder. The glass used was in the form of thin sheets, in some cases curved (spherical), and in others plane. Each of these factors would have an influence on the thickness of film obtained, as would also the temperature and vapour pressure at which the film was formed. Some typical results obtained for the film thickness are given in the following table:—

Table I.—*Film Thickness Values.*

No.	Nature of material.	Film thickness.	Investigator
1.	Glass globes	0·0000033	Ihmori
2.	Cotton silicate (glass-wool)	0·0000133	Parks
3.	Sand (microscopic powder)	0·00000045	Briggs
4.	Quartz (very fine powder)	0·0000013	Katz
	Anorthite (as above)	0·0000062	Katz
5.	Glass (incandescent lamp globes	0·00000166	Langmuir

There are two theories regarding the formation of a film on a solid. According to the first the force acting is physical in its nature, and the intensity of its effect varies inversely as some power of the distance between the two molecules concerned. The force is similar to the force of gravitation, but acts through the distance between molecules. According to this theory successive layers of molecules may be built up on the surface of a solid to a thickness such that the attractive force of the solid just equals the tendency of the outer layer of the film to evaporate.

The second theory assumes that a chemical reaction takes place and that the water taken up becomes a part of a more or less stable chemical compound. According to this theory a variable amount of water could be taken up by solids depending only on the capacity of the solid to form a loose compound with it.

The second theory has usually been assumed to hold for the film of water forming on glass surfaces, free or loosely combined alkali present in the glass, being the substance with which the water reacts. Ihmori (*loc. cit.*) found that keeping the glass in boiling water for some time decreased the amount of water which it would take up. He believed that alkali was removed during this boiling, and that the decrease in the amount of moisture taken up was due to this fact.

It seemed worth while to check the values obtained using glass and sand, having known surfaces, if possible. Since no work has been done to determine the thickest film which can form without free liquid appearing, a method of doing this was worked out. This film was compared with the film formed with other liquids to see whether there was any basis for the thery that a chemical compound formed with water.

* From the *Journal of the American Chemical Society*, xli., No. 4.

Materials.

Solids ; Sand.—Ordinary river sand was used. It was treated with conc. hydrochloric acid until no test for iron was shown. The acid was then washed out with distilled water and the sample dried in the air. Four samples were obtained by sifting. The first sample contained all of the sand which passed the 10-mesh screen but was retained by the 20-mesh screen. The second, third, and fourth samples consisted of the fractions from the original lot retained by the 40-, 60-, and 80-mesh screens respectively. These are called 10-, 20-, 40-, and 60-mesh sands in thi paper.

The grains in this lot of sand were far from spherica no two diameters being the same. An approximation of the surface was obtained by weighing a counted number of grains (4000 to 5000), to get the average weight per grain, and determining the specific gravity. On the assumption that the grains were spherical the diameter and surface of a single grain could be calculated. It was realised when these values were obtained that they were at best only approximations.

Ottawa Sand.—A single sample of sand called in this paper "Ottawa Sand," consisted of well-rounded grains. This sample gave values by the above mentioned method which were very close to the true value for the diameter and surface. It was considered to be of known surface.

Glass Pearls.—The glass pearls used were solid, round, and of various sizes, as indicated in the table below. A few, which were poorly formed, were removed from the lot by rolling them down an inclined board. Those which were not round could be easily picked out in this way. The pearls were from two different sources, and apparently of different kinds of glass. They differed considerably in specific gravity.

The first lot was purchased at retail. The material was sold under the name of "Glistening Dew" and was used to decorate fancy cards, Two samples were obtained from this lot by "elutriation." A quantity of the pearls were placed in a tube and delivered from it at a slow rate into a rising column of water. Under these conditions by properly regulating the current the lighter ones were carried up and the heavier ones sank to the bottom. These samples are No. 9 and No. 10 in the tables.

The second lot consists of 5 samples, Nos. 1, 3, 5, 7, and 8. The individual pearls in each sample were of the same diameter except for No. 7, which contained pearls of two sizes. These samples were obtained from Germany, and when received were coated with dye.

All of the samples were cleaned by boiling in conc. nitric acid, washing free from acid, and air drying. The diameter, surface, and volume of the pearls in each lot were determined by the method used for the sand.

Liquids.—Distilled water and a series of organic liquids were used to form the films.

Specific Gravity of Solids.—The specific gravity of the sand and the pearl samples was determined by displacement of water. A specific gravity bottle was weighed, empty, full of water, and then with a known weight of sample substituted for a part of the water. To avoid air bubbles the weighed sample was run into water in a fine stream. The bottle was then placed in a partial vacuum and let stand for several hours before the final filling and weighing was done.

Method of Determining Film Thickness.—In most of the previous work done on determining film thickness the film has been formed by subjecting the sample to the vapours of water and establishing an equilibrium at the contact surface. Usually the water vapour was at or near its saturation point. As a check on the results obtained in this way the method used in this paper was evolved, which consists in getting an equilibrium of the film, by the use of liquid water rather than vapour, and getting it with the air saturated. This would give the maximum film which could form, and at the same time would, by the magnitude of the results obtained, indicate whether there

was an essential difference between a film formed from the vapour and one formed from the liquid.

Considering the sand and pearl samples already described, the method involves the addition of small amounts of liquid to them, thus gradually building up on them a film of water. As successive layers of molecules are added to this film a thickness is finally reached at which the surface molecules act as normal molecules. That is they evaporate, flow, exert surface tension, &c. Any liquid beyond this amount would remain in the liquid condition. It was only necessary to get a definite test for the point at which these new properties exhibit themselves.

Apparatus.—The first and simplest arrangement used or this purpose consisted of a burette and an Erlenmeyer

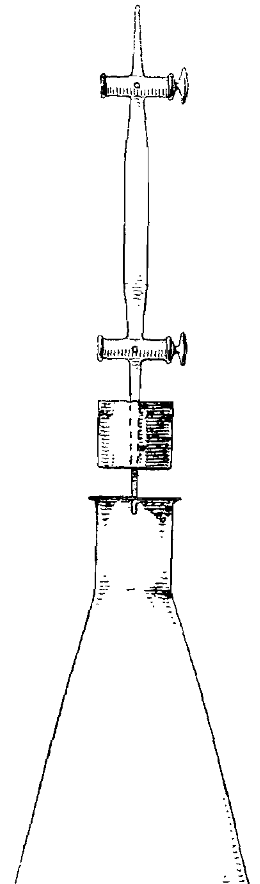


Fig. 1.

flask. The weighed sample of sand was placed in the flask and liquid added from the burette a drop at a time, with thorough shaking between, until a final drop caused the grains to stick to the flask. When this occurred water was present as free liquid. This "sticking point" was taken as the end-point of the titration.

An ordinary burette soon proved unsatisfactory for delivering the liquid, especially so in cases where the liquid was volatile. Delivering the liquid into an open flask also introduced errors with these liquids. To avoid these losses due to volatility of the liquids, and to limit definitely the volume of air saturated during a titration, a weight burette, Fig. 1, was substituted for the ordinary burette and the liquid was delivered into a closed flask.

Procedure.—In carrying out a single determination the following procedure was used :—200 grms. of the air-dry sample was weighed and transferred to the clean dry Erlenmeyer flask. The flask was then closed by means of the stopper carrying the weight burette. The liquid was run in a drop at a time, the sand being thoroughly shaken after the addition of each drop. Towards the end of the titration only fractions of a drop were added, these being removed by tipping the flask to bring the pearls in contact with the tip of the burette.

A final addition of liquid caused a large number of the pearls to stick to the walls of the flask. The weight of the liquid used gave the amount of liquid taken up when a film of maximum thickness formed. Corrections were made in the case of volatile liquids for the amount of liquid necessary to saturate the air in the flask under the working conditions.

After a determination in which sand was used the sand was air-dried and then heated to strong redness in a large platinum dish. After partial cooling it was transferred to a desiccator over phosphorus pentoxide, and kept for future determinations. The pearl samples were not ignited. They were boiled with strong nitric acid, to which some hydrochloric acid was added and were air-dried after being washed free from acid.

This procedure was followed for the purpose of determining whether a chemical reaction was involved in the holding of the liquid. If the pearls were air-dried there would be much less tendency for an unstable chemical compound to be broken down than if they were dried *in vacuo*. The intention was to have the chemical compound, if it formed at all, present at the time of titration, and not formed during it. It seemed improbable that any chemical compound formed by the methods used would decompose on exposure to ordinary conditions of temperature and pressure.

(To be continued).

OFFICERS' GUIDE TO CIVIL CAREERS.

"Officers' Guide to Civil Careers" is the latest bookstall pamphlet in the series issued by the Ministry of Reconstruction.

After warning employers to beware lest through their excess of caution about employing new men the best brains of the country should be tempted abroad, the pamphlet explains clearly to those seeking employment that military pay is no criterion of civil life value, and that a man must consider what his qualifications and abilities for the career he proposes adopting really are, in order to avoid setting an excessive and prohibitive value upon his services.

While many officers on demobilisation will step straight back to their work, it is obvious that the great majority will need some form of assistance to enable them to make a fair start in civil life. As suitable appointments cannot at once be found for everyone, and some may have to wait for some time before their chance comes, prudence in the disbursement of gratuity and savings is very advisable, and it is strongly urged that they should be regarded, not as pocket money, but either as capital or as an emergency fund to be drawn upon until regular work is obtained.

In addition, the Military Service (Civil Liabilities) scheme, which deals with cases of special hardship arising from service in the Forces, is to be continued for a limited period, and application for assistance may be made under this scheme by any officer or men who, having joined H.M. Forces after August 3, 1914, is unable to meet certain financial obligations and is so exposed to serious hardship, or who having previously had a business

of his own wishes to resume it, the maximum individual grant being £104.

The pamphlet describes the part played by the Appointments Department in helping to solve the Officer problem and gives a complete list of the District Branches of the Department. It gives details, too, of the scheme to provide State funds for the higher education and practical training of officers and men of educational promise.

The contemplated schemes comprise courses of higher education in Universities, Colleges, and other institutions, practical training in offices, works, and professional employments, and agricultural training at colleges or on farms. The annual sum granted will not, save in exceptional circumstances, exceed £50 for fees and £175 for maintenance.

There ie also a certain limited number of appointments under the State and Local Authorities which may be suitable for ex-officers possessing special qualifications, and the main classes of such appointments and the various methods of selection are indicated.

In a section entitled "An A.B.C. of Occupations" an attempt on new lines is made to provide a brief account of a large number of professions and industries, indicating the sort of qualifications required and as far as possible the prospects offered. A section is also devoted to Overseas openings. The pamphlet, in short, seeks to give an ex-officer information or to put him on the track of information on every matter that touches on the problems of his re-settlement.

Referring to Chemistry it says :—

"This is one of the sciences on which depend many of our great manufacturing processes, such as the 'smelting' or extraction of metals from their ores and their subsequent refinement; the production of gas from coal; the manufacture of the acids; the vulcanisation of rubber; the preparation of tans for the tanning of hides; brewing; the fermentation industries and the manufacture of sugar, jam, biscuits, cattle food, soap, margarine, explosives, and artificial manures, to name but a few. There is thus a highly important chemical side to a large number of industries, for each of which a special branch of chemical technology is required. The case of dyeing is specially significant. Before the war Germany had organised the industry to a high state of perfection and exercised a virtual monopoly. The attempt to reorganise the British industry is supported by the Goverment, who have assisted a company known as 'The British Dyestuffs Corporation, Ltd.' It is estimated that it will take fully ten to fifteen years to reach a position even approaching that of the Germans, which was won by very hard work, by great patience, by paying close attention to the wants of their customers, and by spending large sums of money on research. For any branch of chemical industry a study of the pure science is almost indispensable. Starting from the matriculation standard, three years is normally required to obtain a B.Sc. or similar degree or diploma in chemistry, a knowledge of at least the elements of one or two other sciences being required at the same time. The minimum cost of training and maintenance may be put at about £200 a year, and the prospect is offered to any man of ordinary ability of securing an appointment on completion of his studies worth £200 to £300 a year to start with. Many chemical students who have served in the Forces seem reluctant to complete their interrupted training. The Institute of Chemistry emphatically advises them that their chances of success will depend largely on adequate preparation."

The New Transport Company, Ltd., announce two meetings at the Caxton Hall, Westminster, S.W. 1. On Monday, June 30, at 8.30 p.m., Mr. A. W. Gattie will give an Address on his "System of Cheap Transport." On Monday, July 7, at 8.30 p.m., Mr. Roy Horniman will speak on the "Transport Bill and Housing Bill."

BOARD OF TRADE ANNOUNCEMENT.

Opening Credits on Behalf of Enemies.

The Board of Trade have issed a General Licence under the Trading with the Enemy Proclamations authorising persons in the United Kingdom to open credits on behalf of persons or bodies of persons in enemy countries for the purpose of financing transactions that have been authorised under the trading with the Enemy legislation in the United Kingdom or any other part of His Majesty's Dominions, and transactions between persons residing or carrying on business outside His Majesty's Dominions which have been authorised by the Allied and Associated Governments or any of them.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 4, 1919.

Dr. Samuel Rideal, President, in the Chair.

Certificates were read for the first time in favour of Capt. John Dalton and Mr. William Norman Leng.

Certificates were read for the second time in favour of Mr. Andrew More, F.I.C., John Haworth, F.I.C., and Henry Turner Lee, M.Sc., A.I.C.

The following were elected members of the Society :— Messrs. Charles Frederick Lee Barber, A.I.C., George Stanley Withers Marlow, B.Sc., F.I.C., and Frederick William Read.

The following papers were read :—

"*Examination of Commercial Samples of Nicotine.*" By Percival J. Fryer, F.I.C.

The author gives a review of the existing methods for the estimation of nicotine, followed by special remarks upon the refractive index as a means of estimating the amount of water present in nicotine solutions, whether the nicotine exists free or as oxalate or sulphate. The question of other possible and likely adulterants is also considered and briefly discussed.

"*Mexican Insects in Poultry Food* (Notonecta, Corixa, *and* Mexican Cantharides)." By T. E. Wallis, B.Sc. (Lond.), F.I.C.

Certain poultry spices and foods contain insects either whole or powdered; these have been identified as consisting mainly of species of *Notonecta* and *Corixa* coming from Mexico. These insects form a regular article of commerce, and have also been sold under the name of "Mexican Cantharides."

Photographs, drawings, and descriptions of the insects are given, which will enable the analyst to identify them whole or broken.

"*A Rapid Method for Determining Nickel and Cobalt in Ores and Alloys.*" (Part III.). By W. R. Schoeller, Ph.D., and A. R. Powell.

In this, the last paper of the seriea, the estimation of nickel and cobalt in various alloys is described. They are precipitated by adding solid potassium iodide to a strongly ammoniacal tartrate solution. Manganese is estimated colorimetrically in the cobalt precipitate if in small quantities. If there is much manganese it must be eliminated by precipitating the nickel and cobalt as sulphides or xanthates.

"*Note on the Oil of* Ceratotheca sesamoides." By E. Richards Bolton, F.I.C.

Ceratotheca sesamoides, which grows on the Gold Coast, is closely allied to *Sesamum indicum*. The seeds are very similar, and so are the oils; in fact, all the analytical re-

sults which are given in the paper, with the exception of the Baudouin reaction, which is negative for *Ceratotheca sesamoides*, might be given by sesame oil. The oil would be useful as edible products.

"*An Improved Method for the Estimation of Nitrates in Water by means of the Phenolsulphonic Acid Reaction.*" By ROBERT C. FREDERICK.

Nitrates associated with chlorides up to 100 parts chlorine per 100,000 can be very accurately estimated by using a phenolsulphonic-sulphuric acid mixture made as described. The colour produced by the nitrates, which is very pure, is compared with that produced by a standard ammonia solution.

"*Estimation of Morphine in Indian Opium.*" By JITENDRA NATH RAKSHIT and FRANK J. D'COSTA.

The authors compare results obtained by the lime and polarimetric methods of estimating morphine in opium, and as a result of their experiments they are of opinion that the polarimetric method offers certain advantages.

GEOLOGICAL SOCIETY.

Ordinary Meeting, May 21, 1919.

Mr. G. W. LAMPLUGH, F.R.S., President, in the Chair.

THE following communications were read:—

"*The Silurian Rocks of May Hill.*" By CHARLES IRVING GARDINER, M.A., F.G.S.

The district of May Hill comprises a small area of ashy grits, which Dr. Callaway in 1900 considered to be of Pre-Cambrian age. The evidence now available does not seem to warrant any definite opinion as regards the age of these beds. Llandovery sandstones are extensively developed, and are of Upper Llandovery age. They consist of a lower division of coarse sandstones and conglomerates.

"*The Petrography of the Millstone Grit Series of Yorkshire.*" By ALBERT GILLIGAN, D.Sc., B.Sc. F.G.S.

Since the pioneer work of Sorby on this subject, published in 1859, the clastic deposits of the carboniferous system have been unaccountably neglected by petrologists. The author has followed the usual methods of investigation, and has collected a large number of pebbles and specimens from widely-separated areas which have been examined microscopically. Numerous separations of the heavy minerals have also been made from all types of rock, varying from coarse conglomerates to shales, which occur in the series.

Quartz-pebbles are dominant, and vary much both in size and in colour. The largest are found in the coarse-grained beds at the bottom and top of the series. They often show double-sphenoid forms suggestive of derivation from mechanically-deformed rocks, which inference is shown to be correct by the undulose extinction, the crenulate and mylonised structure seen when sections of them are examined in polarised light.

Blue and opalescent quartz is very common, containing inclusions often of indeterminable character arranged in streams or rows; others contain liquid with movable bubbles, while needles and hair-like inclusions are also usually present. The quartz of the finer material is similar in character, and the inclusions in the grains suggest that it has been originally derived for the greater part from such rocks as gneisses and schists.

Felspar-pebbles are abundant in all the coarse beds. They are dominantly microcline or microcline-microperthite, and, when broken, are found to be perfectly fresh, the lustre of the cleavage-faces being most remarkable. Blebs of quartz are frequently present in these felspars. In many of the rock-sections grains of microcline and oligoclase, quite fresh and unaltered, are common. Fragments showing the intergrowth of blue or opalescent quartz and microcline are fairly abundant.

NOTICES OF BOOKS.

Mnemonic Notation for Engineering Formulæ. With Explanatory Notes by G. FIANDER ETCHELLS. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1918. Pp. 116. Price 6s. net.

THIS book contains the Report of the Science Committee of the Concrete Institute, with many appendices and miscellaneous articles dealing with the use of mnemonic formulæ, with special reference to structural engineering. The general principles governing the selection of symbols are carefully explained, and many suggestions are made which should certainly tend to prevent chaos and confusion in the use of symbols. The author aims above all at following the obvious dictates of common sense, and in all his suggestions has kept specially in view the convenience of the reader; there is undoubtedly much truth in his criticisms of the irrelevance and even misleading nature of some symbols now employed, such as, for example, the use of *Z* for modulus, which he regards as just as logical a proceeding as suggesting the use of M.P. for Georgius Rex. There is possibly an unnecessary amount of repetition in the book, but the author is very anxious to emphasise his points and to make his meaning unmistakably clear, and his main arguments are undoubtedly sound and his points of view entirely sensible.

The Production and Treatment of Vegetable Oils. By T. W. CHALMERS, B.Sc., A.M.I.Mech.E. London: Constable and Co., Ltd. 1918. Pp. xi+152. Price 21s. net.

THIS book on the vegetable oil industries has been written mainly from the engineer's point of view, and the chemistry of the subject is discussed in outline only. The vegetable oil industry is rapidly developing in this country, having made remarkable strides during the last four years, and this book will certainly be welcomed by engineers and others who are finding employment arising out of its development. Although we are not yet entirely independent of foreign countries for manufactured products we are progressing favourably in that direction, and British-made margarine, for example, is now competing very successfully with the foreign product. The book provides very full and well illustrated accounts of the preparatory machinery employed in the treatment of nuts and seeds before they are taken to the oil mill proper, and oil processes of different types are described, as well as methods of extraction by chemical solvents. The advantages and disadvantages of the latter process are fully discussed, and special care is taken to refute the objections which have been raised against it and to emphasise its possible advantages. The refining of oils is treated shortly, very few accurate details of the processes employed being known outside the actual works where they are carried out. The commercial preparation of hydrogen is fully discussed in the chapter on the hardening of oils, and there is much new material in this part of the book. Short discussions of soap manufacture and the recovery of glycerin occupy the last chapers of a book which is a valuable contribution to technical literature.

The Manufacture of Aluminium. By J. T. PATTISON, F.C.S. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1918. Pp. viii+104. Price 7s. 6d. net.

THERE appears to be every likelihood of aluminium finding extensive application in the future, and as improved and cheapened methods of production are worked out and the price of the metal falls there can be no doubt that it will be used very much more universally than it is at present. The author of this book has had exceptional opportunity of making himself acquainted with modern

methods of preparing the metal, and the results of his experience will be exceedingly useful to chemists in similar positions who have still to acquire his knowledge and skill. He gives an interesting account of the evolution of modern processes from the time of Davy's earliest achievement in decomposing alumina to the Heroult and Hall processes, by which almost the whole of the world's output of the metal is now obtained. Precise details are given of the extraction of the metal by these methods, and the properties and preparation of the most important alloys are fully described, a very useful table showing the composition and uses of all the common alloys containing aluminium being included. About half the book is devoted to detailed accounts of methods of analysis employed in the study of the raw material of the aluminium industry and the commercial metal and its alloys. Those methods which in the author's experience have proved most satisfactory as regards quickness and accuracy, are described in full, and there should be no difficulty in successfully carrying out the tests and estimations, of which complete details are given.

Boiler Feed Water. A Concise Handbook of Water for Boiler Feeding Purposes. By PERCY G. JACKSON, F.I.C. London: Charles Griffin and Co., Ltd. 1919. Pp. ix+97. Price 4s. 6d. net.

IN the above modest little handbook the author sets out the results of his experiences as chemist to a Boiler Insurance Company; the material is therefore of a thoroughly practical character. In an introductory chapter the most common difficulties that are met with in the case of boiler plants are clearly explained, and the work begins with a summary of the mineral constituents of feed water and its more frequent contamination. Corrosion, a most serious danger in boilers, is discussed exhaustively, and this is followed by a chapter on Softening—Analysis of Water and of Boiler Scale. Other practical details are given, and the book concludes with an appendix of factors and other useful data. There is a good index, and the author is to be congratulated in having condensed a very large amount of sound practical information into a small bulk.

Reports of the Progress of Applied Chemistry used by the Society of Chemical Industry. Vol. III. 1918. Society of Chemical Industry, Central House, 46-47, Finsbury Square, E.C. 2.

THIS volume contains the reports on Agricultural Chemistry and Foods from the literature of the past three or four years, together with much other useful information. There are twenty-two important articles on various subjects by specialists in the particular industries, all of which are good. It is not possible here to refer to each, but Glass Refractories, by W. J. Rees, F.I.C., Metallurgy of Iron and Steel, by C. O. Bannister, F.I.C., and the Metallurgy of the Non-ferrous Metals, by G. Patchin, A.R.S.M., are of very great value at the present moment when so much development is taking place in these industries. Reports on Ceramics, Building Materials, and Fermentation are promised for the next volume, which will be awaited with interest.

NOTES.

METRIC SYSTEM IN BELGIUM.—The local Syndical Chamber for machine tools, industrial products, &c., of Liège is complaining of the difficulties caused by the almost universal British habit of quoting for goods in other than metric measures. The honorary British Vice-Consul at Liège is repeatedly having his attention drawn to the same subject, and he points out that if United Kingdom firms wish to develop their trade in Belgium quotations under the metric system are essential.

AT the Annual General Meeting of the Institution of Gas Engineers, held recently at the Institution of Civil Engineers, some remarks by Prof. Smithells on the application of Science to Industry are of such wide importance that we take the liberty of reproducing them. Referring to Scientific Principles and Practical Problems he said:—"The particular question with which I am concerned is how we shall provide the knowledge of scientific principles and their application to practical problems. It is here that I and my tribe come into relationship with the industrial world; and it is here we are apt to come into conflict. On the one hand, we have the practical man impressed with a knowledge of the realities of industry, of the immense importance of the factor of experience, of the value of native talent and sagacity—what you may almost call moral qualities—of the futility of certain kinds of learning, and of the dangers of the eager theorist. You have this practical man bent on getting what he regards as necessary from science on the strictest terms of economy in time, and with the least possible interference with what he looks upon as the real business of learning one's trade. We, on the other hand, stand with our knowledge of science, with our experience of its power of furnishing humanity with new resources, with our desire that it shall shed its full light into every corner, and with the record before us of what it has achieved for industry. We are in danger, not I think of over-estimating what it has to offer, but of under-estimating how much there is besides science which is indispensable for success in industrial callings, and our tendency is, perhaps, to undervalue education which is inherent in the prosecution of the practical calling itself. Every industry, and the gas industry among the number, can no doubt show examples of men who have by self-teaching equipped themselves with a remarkable knowledge and grasp of scientific principles. Such examples are very impressive; but I believe they have their disadvantage in tending to elevate into a prescription for all what is possible only to the very few. I think it is no exaggeration to say that at the present time you may see abundant examples in British industry of the insufficiency of self-education in science—cases where a knowledge of science and the power of using it have to some extent been acquired, but where want of the firm ground of a knowledge of basic principles is very apt to lead men astray." His remarks upon the Need of Scientific Masters were as follows:—"I think is will be generally agreed that the science teacher must come in to give his aid. And, of course, he has come in. But we must go further. I think the time has come when the gas engineer must recognise that the modern conditions of his industry demand a very much more extensive and thorough scientific training than has hitherto been customary. It is not right that I should prophesy who are going to be the highest powers for good in advancing the gas industry—the man of affairs, the manager, the engineer, or the chemist. But I think that no one can doubt that the industry does need, and will need more and more, an accession to its ranks of men who are really scientific masters of their profession. The science that ministers to your calling is not less comprehensive than that required for any other branch of engineering. The mechanical, civil, and electrical engineers feed their profession with a constant stream of recruits who have had a three or four years' course at a University; and I feel certain that gas engineers should come into line. This will no doubt seem a large demand; but I am satisfied that nothing less will suffice. The view that all essential knowledge of science for the gas engineer is to be obtained in spare hours of the working day by study, by attendance at evening classes, or by short intensive courses, cannot be entertained. I have no desire to belittle such forms of education. They may be made good and useful so far as they go; but they cannot possibly provide all that is needed. I would most earnestly entreat the members of the industry not to be beguiled by half-measures, but to make bold educational investments. I do not look for a sudden change of

attitude, nor do I expect to exercise much influence on a great many individuals. I do not foresee a rush to the Universities; but I do sincerely hope that those who have the faith and courage will make a beginning upon a real professional education conformable to the needs of the industry and the present state of scientific knowledge."

CANADIAN NATIONAL EXHIBITION AT TORONTO.—Information has been received from His Majesty's Trade Commissioner at Toronto (Mr. Field) to the effect that it is proposed to obtain space at the Canadian National Exhibition, to be held at Toronto during the last week of August and the first week of September next, for a Bureau of Information in connection with the Trade Commissioner Service in Canada. Mr. Field has expressed a desire to display the catalogues and other trade publications of United Kingdom firms at the Bureau in question, and it is suggested that catalogues, &c., of the following lines would be useful for the purpose:—Textile machinery; crockery, glass, &c.; industrial machinery, including pulp and paper machinery, and supplies; electrical machinery, appliances, and equipment; shipbuilding machinery and supplies; mining machinery and supplies; heavy machine tools; electrical railway equipment; motor vehicles; chemical plant, &c.; scientific instruments; sugar machinery. Manufacturers and others who wish to avail themselves of this opportunity of having their catalogues brought to the notice of Canadian firms at the Exhibition should communicate with Mr. Field direct, enclosing copies of their catalogues and other trade publications for display at the Bureau at the above-mentioned Exhibition. The catalogues, &c., should be received by Mr. Field—whose address is 257—260, Confederation Life Buildings, Toronto—not later than August 15 next.

DIAMONDS were discovered in Brazil in the year 1728, and since that time until the present intermittent supplies of Brazilian diamonds have been secured, chiefly from river washings. It has recently been reported that the source of these stones has been traced to "pipes" similar in character to the well-known African deposits; one pipe is reported to be several square miles in extent! A company has been formed to work the property, and the results will be looked forward to with interest.

THE export of zirconia from Brazil to the United States, Great Britain, and Japan has grown very considerably; the figures for 1918 show an export of 2,141,182 kilos.

CASEIN WATERPROOF GLUE.—(H. A. Gardner, *Aircraft Technical Note* No. 46, Navy Department, U.S.A., Bureau of Construction and Repair).—The Forest Service has recently completed some very extensive tests with casein glue. These tests have demonstrated that there are now available, commercially at least, three brands which are all furnished by the makers in the form of dry compounds to be mixed with water. These glues are to be considered waterproof in the sense that they are not dissolved out or injured by water. Permanently prolonged soaking causes such glues to soften and become weak, but upon subsequent redrying they regain their former strength. The principal difficulty with these glues is in their rapidity of setting after being mixed with water; from two to five hours is the longest period of fluidity. Experimental batches of casein glue, to which certain materials have been added to delay the set, have, however, remained fluid and workable for periods as long as forty-eight hours. Attempts have been made to determine what percentage of bad joints would occur in using casein glue. Every one of about 200 specimens made by ordinary mechanics was found satisfactory. It is believed that, if the instructions of the manufacturers are followed, casein glue is a safer material for aircraft construction than hide glue. It appears, therefore, for strength members in aeroplanes, that these glues should be used in place of hide glue.—*Journ. Franklin Institute*, May, 1919.

Assistant Assayer (aged 23 to 27) required at once. Experience in Assaying Gold and Silver essential. Permanency; good prospects. State age, experience, and salary required.—Address, "A 23," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist, three years' experience in large Tar Products Works before taking active service, now demobilised, desires Employment in London or the Provinces.—Address, T. T., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist wanted for Cotton Dyeing and Mercerising establishment in Scotland. State experience, age, and salary expected.—Address, C. D., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted in a London Laboratory, a Junior Chemical Assistant. Give particulars of training and salary required.—Address, "A.," CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Youth (17), good knowledge of Chemistry, seeks Employment in Laboratory.—Address, A. H., 1, Phœnix Lodge Mansions, Hammersmith, W.

Young man (31), with good knowledge of Chemistry and Engineering practice, desires Situation at living wage with Chemical Engineering firm, or Assistantship in Works Laboratory of progressive firm which appreciates intelligent and willing service.—Address, Sharpe, 7, Toll Road, Kincardine on-Forth.

BIRKBECK COLLEGE, LONDON.

ASSISTANT LECTURER IN CHEMISTRY.

The Governing Body invite applications for the above appointment. Commencing salary £220 to £250 (according to experience and qualifications), with regular increments. —Applications to THE SECRETARY, Birkbeck College, E.C. 4, from whom further particulars may be obtained.

UNIVERSITY OF ABERDEEN.

CHAIR OF CHEMISTRY.

The CHAIR OF CHEMISTRY, in the patronage of the University Court, becomes vacant by the resignation of Professor SODDY on September 30th next. The salary is £900 per annum.
Applications for the office, together with 16 copies of testimonials, should be lodged with the SECRETARY of the University on or before JULY 5th.

STAFFORDSHIRE EDUCATION COMMITTEE

BRIERLEY HILL HIGHER EDUCATION COMMITTEE

Applications are invited for the Post of HEAD MASTER of the Technical School, Brierley Hill, South Staffordshire.
Experience in Teaching and acquaintance with the Iron and Steel Trades, or with the Chemistry of Refractory Materials, desirable.
Initial salary £300 a year.
Further particulars and forms of application may be obtained from the undersigned. Applications must be received not later than JUNE 30, 1919.

GRAHAM BALFOUR,
County Education Offices, Director of Education
Stafford, June, 1919.

If in good condition, Sixpence per copy will be paid for any of the undermentioned numbers of the CHEMICAL NEWS which may be forwarded to this office:—

3052, December 6th, 1918.
3066, January 17th, 1919.
3068, January 31st, 1919.
3069, February 7th, 1919.
3070, February 14th, 1919.
3075, March 21st, 1919.

16, NEWCASTLE STREET, FARRINGDON STREET, LONDON, E.C. 4.

THE CHEMICAL NEWS

VOL. CXVIII., No. 3089.

THE ALLOTROPY OF CARBON.

By MAURICE COPISAROW.

THE application of the theory of allotropy (see CHEMICAL NEWS, cxviii., 265) propounded in general terms for all the elements, to a single characteristic case—the element carbon necessitates our dealing with the valency of the carbon atom and the complexity and varieties of the carbon molecules.

In the light of the chemistry of carbon compounds the carbon atom can be regarded as potentially always tetravalent, as carbon monoxide, carbon compounds containing double or triple bonds, the triphenyl methyl series, and the poly-methylene group in no way undermines the conception of such potential tetravalency.

The polyatomicity of a carbon molecule is proved by—

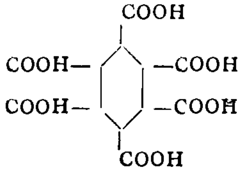
1. The existence of several forms of carbon, chemically and physically distinct from one another.
2. The high v latilisation-point of carbon.
3. The general theory of the solid state.
4. Products of moist oxidation.
5. Combustion of carbon (Rhead and Wheeler, *Trans.*, 1910, xcvii., 2181; 1911, xcix., 1140; 1913, ciii., 461).
6. The X-ray spectro-metric study of the modifications of carbon (Debye and Scherrer, *Phys. Zeit.*, 1916, xvii., 277; 1917, xviii., 291; One and Byl, *Proc. K. Akad. Wetens. Amsterdam.*, 1917, x x , 920 .

Not only has the polyatomicity of carbon molecules been assumed, though more or less tacitly, but attempts have also been made to study the complexity of the molecules and to establish the constitutional molecular formula of one or more of the forms of carbon.

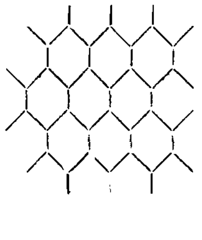
Kekulé (*Zeit Angew. Chem.*, 1899, p. 950) regards a molecule of amorphous carbon as consisting of 12 atoms.

Barlow and Pope (*Trans.*, 1906, lxxxix., 1742) suggested the possibility of a tetrahedron and triphenylene configuration for a carbon molecule (see Figs. 1. and 4*a*).

Dewar (CHEMICAL NEWS, 1908, xcvii., 16) proposed a concentric ring formula, somewhat modified by Redgrove and Tomlinson (CHEMICAL NEWS, 1908, xcviii., 37). Dewar based his view on the moist oxidation of amorphous carbon to mellitic acid—



Aschan (*Chem. Zeit.*, 1909, xxxiii., 561), criticising Dewar's suggestion, put forward a formula, which can be regarded as an extension of the triphenylene representation by Barlow and Pope (*loc. cit.*)—



Dimroth and Kerkovius (*Ann.*, 1913, cccxcix., 120) conclude from their study of the oxidation of carbon the carbon molecule to consist of pentagons as well as hexagons.

Bragg (*Proc. Roy. Soc.*, 1913, A, 610), studying the crystalline structure of diamond by means of the X-ray spectrometer, advanced a three-dimensional configuration for the structure of the diamond (see Fig. 2).

(In connection with the X-ray spectrometric method of investigation of crystalline structures attention may be drawn to the work of Moseley—*Phil. Mag.*, 1913, VI., xxvi., 1024; 1914, VI., xxvii., 703; Barlow—*Proc. Roy. Soc.*, 1914, A, 623; and Ewald—*Phys. Zeit.*, 1914, xv., 309).

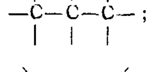
Hans Meyer (*Monats.*, 1914, xxxv., 163), discussing the carbon "molecule," puts stress upon the difficulty, if not futility, of trying to define the chemical entity of the three forms of carbon.

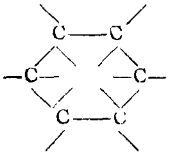
Debye and Scherrer (*loc. cit.*) conclude from the Lauegraphs of their modified X-ray spectrometric method of study, that diamond and graphite are the only two distinct forms of carbon, amorphous carbon being apparently simply finely divided graphite. They assign a tetragonal configuration to diamond and a trigonal to graphite. It is clear from the above that a method of investigation so general as to be applicable to all forms of carbon has not yet been proposed.

Whilst the method of moist oxidation can be applied more or less successfully to amorphous carbon and to some extent to graphite, the X-ray method is confined to diamond with a somewhat strained extension to graphite.

Now, if we consider the problem from the point of view of linkages, *i.e.*, of molecular structure in the light of the theory of allotropy, we secure a general method of investigation, embracing all forms of carbon, a method capable of extensive experimental verification on the basis of all the known chemical and physical properties. Investigating all possible representations of the structure of a carbon molecule we find that these possibilities resolve themselves into three fundamentally distinct classes or groups.

I. A *non-rigid* molecular configuration, some valencies of which are *free*—





(See also Fig. 1).

II. A *rigid* molecular configuration, some valencies of which are *free* (see Fig. 3).

III. A rigid molecular configuration, all valencies of which are *fixed* (see Figs. 4*a*, 4*b*, and 2).

Thus on theoretical grounds we expect to find in the case of carbon not more than three distinct allotropic forms, a conclusion in striking agreement with facts; *i.e.*, the existence of three forms of carbon—amorphous carbon, graphite, and diamond.

The several new modifications (graphitoid, &c.) of carbon suggested by Brodie, Berthelot, Luzi, and others have been proved to be either compounds or solutions and mixtures of carbon with some other elements.

(See Porcher, CHEMICAL NEWS, 1881, xliv., 203. Bartoli and Papasogli, *Gazz.*, 1882, xii., 113; 1883, xiii., 37; 1885, xv., 445. Moissan, *Comptes Rendus*, 1893, cxvi., 609; 1894, cxix., 976; 1895, cxx., 17; cxxi., 540; *Ann. Chim. Phys.*, 1896, VII , viii., 289, 306, 466. Wiesner, *Monats.*, 1892, xiii., 371. Weinschenk, *Zeit. Kryst. Min.*, 1897, xxviii., 291. Hyde, *Journ. Soc. Chem. Ind.*, 1904, xxiii., 300. Trener, *Jahresb. Geolog. Reichs. Wien.*, 1906,

405; *Zeit. Kryst. Min.*, 1909, xlvi., 124; Charpy, *Comptes Rendus*, 1907, cxlv., 1173; 1909, cxlviii., 920. Le Chatelier and Wologdine, *Comptes Rendus*, 1908, cxlvi., 49).

Debye and Scherrer's (*loc. cit.*) unification of amorphous carbon with graphite is untenable as it is in complete disagreement with all the chemical and physical properties of these two forms. No matter how finely divided the graphite may be (Acheson's or "colloidal" graphite) its behaviour towards moist oxidants, its products of oxidation, mode of combustion, and physical properties all greatly differ from those of amorphous carbon.

Kohlschutter's (*Zeit. Anorg. Chem.*, 1919, cv., 35, 121) effort to prove amorphous carbon and graphite to be physical forms of "black carbon," thus agreeing with Debye and Sherrer's (*loc. cit.*) conclusion, appears to be decidedly strained, ignoring as it does the more distinct chemical and physical differences of these two forms of carbon, the conditions of transition and the possibility of the "intermediary stages" being simply mixtures of graphite with amorphous carbon.

H. Meyer (*loc. cit.*) and H. Meyer and Steiner (*Monats.*, 1914, xxxv., 475), recording the dependence of the yield of mellitic acid from charcoal upon the latter's source and temperature of carbonisation, express some doubt as to the entity of the carbon "molecule" and the close connection of its constitution with the product of oxidation.

But we must remember that deductions depend often more upon the character of interpretation of certain experiments than the experimental evidence itself. The yield of mellitic acid *does* vary with the source of the charcoal employed and the temperature, pressure, and duration of carbonisation, but the formation of the mellitic acid cannot be attributed to the presence of complex hydrocarbons, possibly retained by the charcoal carbonised at a comparatively low temperature, as a quantitative determination of the percentage of hydrogen, oxygen, and nitrogen invariably accompanying this kind of charcoal gives not more than 1 per cent of these gases, whilst the yield of mellitic acid reaches as high a value as 40 per cent. The dark residue "mellogen" (Bartoli and Papasogli, *loc. cit.*; Dickson and Easterfield, *Proc. Chem. Soc.*, 1898, 163), remaining after the first oxidation, gives on exhaustive oxidation again mellitic acid and also some oxalic acid.

To attribute the varying yield of mellitic acid to the existence of several modifications of amorphous carbon, as some investigators are inclined to do, is quite unwarranted as such an explanation of the somewhat varying quality and properties of charcoal would necessitate the assumption of a whole series of modifications of amorphous carbon, corresponding to every source of charcoal and practically to every 20—50° of temperature of carbonisation.

The causes of the dissimilar behaviour of various samples of charcoal are probably much simpler and nearer at hand. Such causes may be:—

1. A high temperature of carbonisation, which, reducing the porosity of the resulting amorphous carbon or charcoal, increases in consequence its resistance to oxidation.
2. A high temperature of carbonisation facilitates the conversion of amorphous carbon into graphite, so that we may deal with charcoal containing a high percentage of finely divided graphite (Arsem, *Trans. Am. Electrochem. Soc.*, 1911, xx., 105).
3. A high percentage of mineral matter contaminating charcoal may affect its properties in more than one way. Thus we find that there are three distinct allotropes of carbon corresponding to the three, theoretically possible, fundamentally different configurations.

The following considerations may serve as a pioneer attempt to assign to each modification its constitutional formula.

The calorimetric measurements of the heat of complete combustion of carbon per grm.-atom give the following numbers (Berthelot and Petit, *Ann. Chim.*, 1889, VI., xviii., 89, 98):—

	Cals.
Amorphous carbon	97650
Graphite	94810
Diamond	94310

These figures indicate the sum total of the energy liberated during the formation and degradation of the possible complexes (Rhead and Wheeler, *loc. cit.*) plus that of the oxidation of the carbon monoxide to carbon dioxide.

(It must be noted that the calorimetric measurements of the heat of combustion of the modifications of carbon differ considerably with every experimenter. Compare data of Favre and Silberman, *Ann. Chim.*, 1852, III., xxxv., 357; Berthelot and Petit, *loc. cit.*; Mixter, *Am. Journ. Sci.*, 1905, IV., xix., 440; and Roth and Wallasch, *Ber.*, 1913, xlvi., 896).

Taking equal weights of amorphous carbon, graphite, and diamond, and subjecting them to complete combustion, we find that the amount of heat evolved is different for each form of carbon, although the number of atoms taken and the number of CO_2 molecules formed is identical.

Looking for the cause of this dissimilarity of thermic values we are driven to attribute it to the different stability of the molecules in the three cases, which must depend upon the mode of linkage of the units constituting the molecule as well as the complexity of the molecule itself.

Returning to our classification of theoretically possible configurations we expect that the least stability will be exhibited by molecules whose units have the power of free rotation, or, in other words, which have free valencies; the maximum stability will be found in the molecule all the constituent units of which are in a state of rigidity and all valencies fixed; the intermediate case being a molecule having some valencies free, but a rigid structure. Now, considering the fact that the greater the stability the smaller will be the evolution of heat on complete combustion (compare the case of phosphorus), and correlating this with the calorimetric measurements quoted above, we find that—

Amorphous carbon is represented by Class I., where *none of the atoms are rigid.*

Graphite, Class II., the atoms are *rigid* but some valencies free.

Diamond, Class III., *all* atoms are rigid and all valencies fixed.

These deductions find strong support in the character of the products of the moist oxidation of carbon.

The molecule of amorphous carbon with none of its units rigidly fixed, as might be expected, is the least resisting to oxidants and yields mellitic acid. Graphite with its partially fixed units gives rise to graphitic oxide or acid, an acid more complex than mellitic. The rigidly fixed units of diamond are practically unaffected under the same conditions of oxidation. (V. Meyer—*Ber.*, 1871, iv., 801; *Ann.*, 1875, clxxx, 175. Schulze—*Ber.*, 1871, iv., 802, 806. Standenmaier—*Ber.*, 1898, xxxi., 1481; 1899, xxxii., 1394, 2824. Dickson and Easterfield—*loc. cit.* Meyer and Steiner—*loc. cit.*).

It would appear to be very probable, on the basis of the theory of the constitution of the three types of carbon advanced above, that the values of any selected physical property should show a regular gradation from amorphous carbon to the diamond, the value for graphite lying between the values for the two other forms. If we find that such a gradation appears when a number of physical properties are taken, we can say that this behaviour is consistent with the hypothesis on which the present discussion is based, and it may therefore in this sense be regarded as affording evidence confirming the hypothesis.

Below are collected the values for a number of physical constants, which have been determined for all three forms

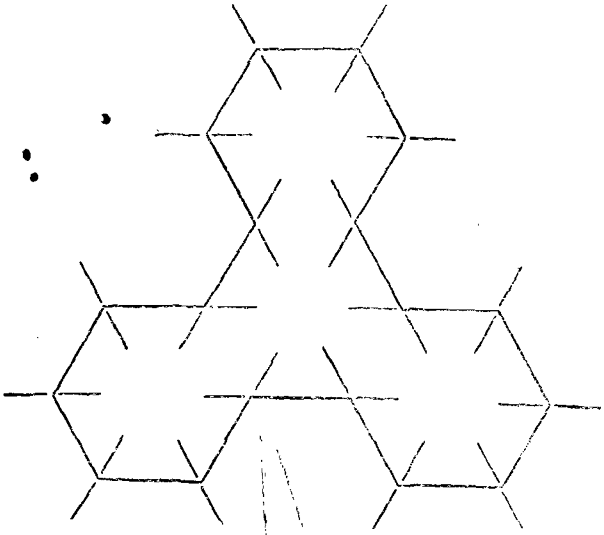


FIG. 1.

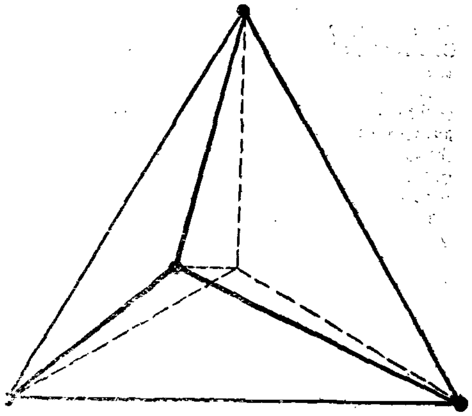


FIG. 3.

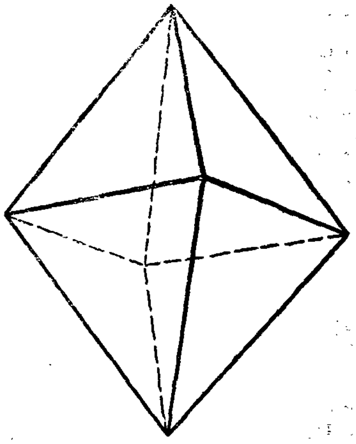


FIG. 4 *a*.

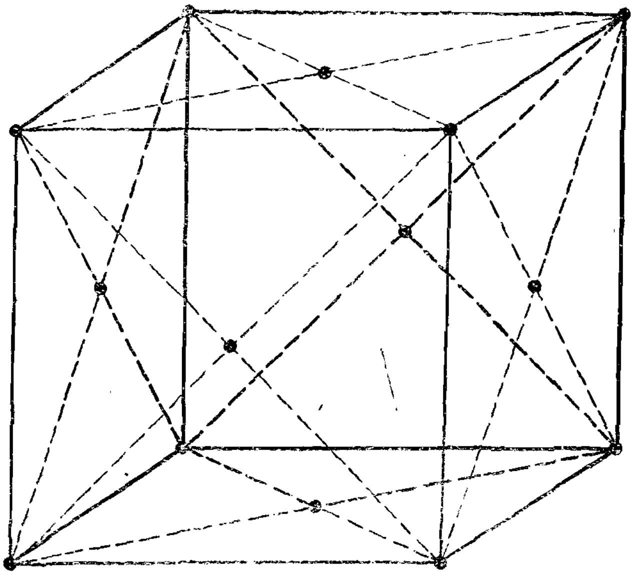


FIG. 2.

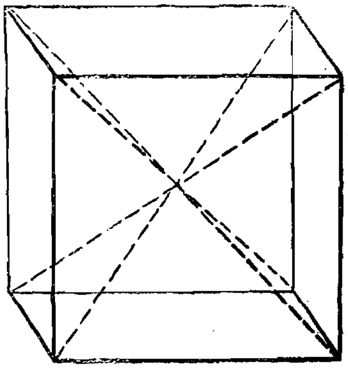


FIG. 4 *b*.

of carbon. The numbers are taken from Landolt Börnstein, "Tabellen," 4th edition, 1912.

1. *Density.*

Diamond	3·51
Graphite	2·10–2·32
Amorphous carbon—	
Gas coke	1·885
Cocoanut-charcoal	1·67—1·860
Lampblack, sugar-charcoal, and wood-charcoal	1·70—1·80

2. *Coefficient of Cubical Expansion.*

Diamond	0·00000375
Graphite	0·0000104
Gas coke	0·0000162

3. *Thermal Conductivity.*

Diamond (0° C.)	0·33 (*a*)
Graphite	0·0117
Charcoal	0·000405

(*a*) Eucken, *Phys. Zeit.*, 1911, xii., 1005.

4. *Specific Heats.*

(All measured by Weber *Pogg. Ann.*, 1875, cliv, 367, 553).

Diamond (10·7° C.)	0·1128
Ceylon graphite (10·8° C.)	0·1604
Wood charcoal (0°—24° C.)	0·1653

5. *Electrical Conductivity.*

Diamond (15° C.)	$0{\cdot}211{\cdot}10^{-14}$
	$0{\cdot}309{\cdot}10^{-12}$
Graphite (15° C.)	$0{\cdot}082{\cdot}10^{4}$
Charcoal (12° C.)	0·25

An inspection of this table shows that, with the single exception of the electrical conductivity, all the physical properties are in the order we should expect. In the case of the electrical conductivity, graphite occupies an anomalous position, in that its conductivity is very much larger than that of either the diamond or amorphous carbon. In this connection two facts appear to be important. First, the value of the electric conductivity of graphite is so very much larger than those of the other two forms that it would lead one to suspect that it is occasioned by something quite different from the mode of linkage of the carbon atoms in the different forms of carbon, since we could scarcely expect that the differences in the atomic linkage would change a substance which is an insulator, like the diamond, into a substance which is a metallic conductor, like graphite. And, secondly, we can see that there is a real anomaly in the case of graphite, because the thermal conductivities are in the order expected, and thence, from the law of Wiedemann and Franz, which states that the ratio of the thermal and electrical conductivities is (at least in the case of metals—Eucken, *loc. cit.*) approximately constant, we should also expect the electrical conductivities to be in the same order.

The abnormal electrical conductivity of graphite is, in fact, a property which still awaits explanation.

The suggested configurations of the allotropes of carbon are also in agreement with the "cyclic condensations" of carbon by Rousseau (*Comptes Rendus*, 1893, cxvii., 164) and Ludwig (*Chem Zeit.*, 1901, xxv., 979; *Zeit. Elektro. Chem.*, 1902, viii., 273), the crystalline structures of diamond and the conclusions of Barlow and Pope (*loc. cit.*), and Bragg (*loc. cit.*), and Debye and Scherrer (*loc. cit.*). The elucidation of the molecular structure of the carbon allotropes throw much light upon the mechanism of the combustion of carbon, a problem which has received a good deal of attention.

Under the stress of experimental evidence the *reduction theory* of Lang (*Zeit. Phys. Chem.*, 1888, ii., 62) has been replaced by that of gradual oxidation by Baker (*Phil. Trans.*, 1888, A, clxxix, 571) and Dixon (*Trans.*, 1896, lxix., 774; 1899, lxxv., 630), which in its turn is being substituted by the *theory of complexes*, proposed by Rhead and Wheeler (*Trans.*, 1910, xcvii., 2181; 1911, xcix., 1140; 1913, ciii., 461).

The conception of a non-rigid configuration for amorphous carbon, containing free valencies, affords a complete explanation of—(1) The comparative easy combustibility of this form of carbon; and (2) The simultaneous evolution of CO and CO_2, products of disruption of the complexes, logically constituting the first stage of oxidation.

The conception of a rigid configuration for diamond and graphite explains the considerable resistance to combustion exhibited by these allotropes, and suggests that no intermediate complexes, assumed in case of amorphous carbon, are likely in the course of combustion of diamond and graphite.

These possibilities present themselves as representing the mechanism of the combustion of diamond or graphite:—(1) Their molecular structures disintegrate at the exceedingly high temperature of its combustion; or (2) It is primarily converted into amorphous carbon (with or without passing through the graphite form in case of diamond, and then pass through the stages indicated for amorphous carbon).

In the light of the work of Moissan (*Comptes Rendus*, 1897, cxxiv., 653), Crookes (*Proc. Roy. Soc.*, 1904, A, lxxiv., 47), and Vogel and Tammann (*Zeit. Phys. Chem.*, 1909, lxix., 598) on the transformation of diamond into graphite, and the work of Berthelot (*Comptes Rendus*, 1902, cxxxv., 1018), Parsons and Swinton (*Proc. Roy. Soc.*, 1908, A, lxxx., 184), and Swinton (*Proc. Roy. Soc.*, 1909, A, lxxxii., 176) on the conversion of diamond into amorphous carbon, the second hypothesis appears to be the more probable one; the transformation of diamond and graphite into amorphous carbon preceding the process of oxidation.

With reference to the combustion of amorphous carbon, whilst the number of theoretically possible complexes is obviously large, the general progress of reaction and final complexes, judging by the ultimate products, can be represented by the equation—

$$2C_x + yO_2 = 2C_xO_y = aCO + (2x - a)CO_2 \rightleftarrows 2xCO_2.$$

Where x is the number of atoms in a molecule of amorphous carbon, y equals $\frac{1}{2}(4x - a)$, and a is a variable, depending upon temperature, pressure, and concentration of oxygen and varying between $2x$ and zero.

A CONVENIENT METHOD OF ANALYSIS OF FLUORSPAR AND OF BASIC SLAGS CONTAINING FLUORINE.

By Lieut. G R. DOYLE.

The author believes that the following method, now published for the first time, will readily commend itself as being in several ways more advantageous than existing processes.

The sample is finely powdered in an agate mortar, and 0·5 grm. is weighed out into a porcelain, silica, or platinum dish. A little water is added to form a paste, and 25 cc. of glacial acetic acid, and the mixture evaporated nearly to dryness on the water-bath, with occasional stirring. The assay is now treated again with 25 cc. of glacial acetic acid, and evaporated completely dry, all free acetic acid being driven off in the steam-oven. The residue is now taken up with a little hot water, transferred to a small beaker, diluted to 80 cc., and boiled for ten minutes, or until the residue on standing a few minutes shows a clear supernatant liquid. If a colour persists, through the presence of acetic acid, the sample is diluted with 20 cc. of water and boiled again.

(Note.—If a large amount of iron be present, or the sample be rather dark in colour, the residue after filtering must be washed back into the previously used dish, and treated again with glacial acetic acid, evaporated to dryness as before, transferred to a beaker, boiled with water, and filtered. The filtrates are combined).

Residue contains:—

(a) All lime existing as CaF_2.
(b) The greater part of the silica.
(c) All iron and alumina.

Filtrate contains:—

(a) Soluble or available lime (CaO and $CaCO_3$).
(b) Soluble silica.
(c) Manganese.
(d) Magnesia.
(e) Lead.

Examination of Residue.

Residue is ignited in a weighed platinum dish (but not so strongly as to decompose CaF_2), cooled, and weighed until constant in weight; treated with HF, and evaporated to dryness on water-bath, ignited, and weighed. Loss = SiO_2.

The remaining residue is increased by 5 cc. H_2SO_4, evaporated until the formation of fumes, and finally ignited and weighed again. Gain = increase of $CaSO_4$ over CaF_2. $CaSO_4 \times 0{\cdot}5735 = CaF_2$.

The residue is boiled for twenty minutes with 20 cc. HCl, transferred to a beaker, increased by ammonium chloride and ammonia, boiled, and filtered. If much Fe and Al are present precipitation is carried out again. The residue of Fe and Al is ignited, weighed, and deducted from the combined weight of Fe+Al+CaF_2. Difference = CaF_2.

If lead be present H_2S is passed before precipitation of the iron and aluminium.

After Fe and Al have been weighed the assay is dissolved, reduced, and titrated, the Al being thence determined by difference.

Examination of Filtrate.

The filtrate is evaporated to dryness with 5 cc. HCl and three drops HNO_3, baked, taken up in 5 cc. HCl, diluted, and filtered. The silica now obtained is added to that found in the residue.

Ammonium chloride solution, bromine to saturation, and excess of ammonia are added to this filtrate, which is boiled, filtered, and, ignited. MnO is calculated from the Mn_3O_4 obtained. Factor, 93·01. (If lead be present it is eliminated by H_2S prior to precipitation of Mn).

The filtrate is increased by ammonium oxalate, boiled, allowed to settle, and filtered. The precipitate, which consists of available lime, is strongly ignited and weighed as CaO.

Magnesia in the filrrate is precipitated with ammonium phosphate, and left overnight to settle.

GALLIUM.*

By L. M. DENNIS and J. ALLINGTON BRIDGMAN.

(Concluded from p. 292).

A STUDY OF CERTAIN SALTS OF GALLIUM.

Gallium Selenate.

A SOLUTION of gallium selenate was prepared by placing gallium hydroxide in an amount of selenic acid insufficient to dissolve all of the hydroxide and heating the acid nearly to boiling. After several hours of digestion the solution was freed from the excess of gallium hydroxide by filtration, and the filtrate was evaporated at room temperature. The crystals that separated were drained on a Witt plate by suction. The salt is very soluble, and it is difficult to obtain crystals that are satisfactory for microscopic examination. The crystals show oblique extinction, and they therefore belong either to the monoclinic or to the triclinic system.

The salt was dried to constant weight in the air and was then analysed. Selenium was determined by placing a weighed sample of the salt in concentrated hydrochlorio acid and heating this to boiling to reduce selenic acid to selenious acid. The selenious acid was then reduced to free selenium by passing sulphur dioxide through the hot solution. The precipitated selenium was collected on a weighed Gooch crucible and was dried at 110° and weighed. Gallium was determined in the filtrate by the sodium sulphite method.

Calculated for $Ga_2(SeO_4)_3.16H_2O$—Ga_2O_3, 21·90; SeO_3, 44·49; H_2O, 33·61. Found - Ga_2O_3, 21·77, 21·66, average 21·71; SeO_3, 44·49, 44·24, average 44·36; H_2O, by difference, 33·98.

* This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by J Allington Bridgman in partial fulfilment of the requirements for the degree of Doctor of Philosophy. From the *Journal of the American Chemical Society*, xl., No. 10.

When the sample of the crystalline gallium selenate was dried in the air 2·5145 grms. of the salt lost 0·2810 grm., which corresponds to 5·94 molecules of water. Consequently, the salt that was dried by suction contains about 22 molecules of water. (The same degree of hydration, namely, 22 molecules of water, was found to exist in a sample of gallium sulphate that was dried by simply pressing the crystals between sheets of filter-paper).

These results indicate that a hydrate of gallium selenate containing 16 molecules of water exists, and that it is also probable that when gallium selenate crystallises from aqueous solution at room temperature the salt contains 22 molecules of water of crystallisation.

The solubility of this air-dried crystalline gallium selenate was determined by placing an excess of the salt in water in a stoppered bottle, heating the contents of the bottle to 25° in a thermostat for six hours and then pipetting off samples of the supernatant saturated solution and weighing them. The gallium in these samples was determined by the sodium sulphite method.

Weight of saturated solution taken (grm.)	0·7558	0·6192
Weight of Ga_2O_3 found (grm.)	0·0908	0·0749

The average of these values is 0·1205 grm. of Ga_2O_3 per grm. of solution. One part of the salt therefore dissolves in 1·74 parts of water at 25°, and 100 cc. of the solution contains 57·58 grms. of gallium selenate.

Cæsium Gallium Selenate Alum.

A solution containing gallium selenate, cæsium selenate, and some free selenic acid was evaporated at room temperature. The crystals were separated from the mother-liquor and were dried in the air. They showed the octahedral form characteristic of the alums.

Cæsium was determined by precipitation with chloroplatinic acid, selenium by precipitation as free selenium, and gallium by precipitation with ammonium sulphite in the filtrate from the selenium determination. The water of crystallisation was determined by drying a sample of the salt to constant weight at about 180°.

Calculated for $CsGa(SeO_4)_2.12H_2O$—Cs_2O, 19·96; Ga_2O_3, 13·31; SeO_3, 36·07; H_2O, 30·65. Found —Cs_2O, 19·78; Ga_2O_3, 13·33; SeO_3, 35·73; H_2O, 30·33.

These results show that the salt has the formula $CsGa(SeO_4)_2.12H_2O$ and that it is therefore a typical alum.

The solubility of this alum in water at 25° was determined in the manner described under the selenate.

Weight of saturated solution taken (grms.)	2·0702	2·0422
Weight of Ga_2O_3 found (grm.)	0·0109	0·0109

The average of these results is 0·0053 grm. of Ga_2O_3 per grm. of solution. One part of the salt therefore dissolves in 24·1 parts of water at 25°, and 100 cc. of the solution contains 4·15 grms. of the alum.

Ammonium Gallium Sulphate Alum and Cæsium Gallium Sulphate Alum.

During the process of extraction of germanium from certain material in this laboratory there were obtained residual solutions that were rich in zinc sulphate, and that contained about 30 per cent of sulphuric acid. Spectroscopic examination of these solutions showed the presence of gallium.

Lecoq de Boisbaudran separated traces of indium from gallium by utilising the fact that ammonium gallium alum is quite insoluble in 70 per cent alcohol (*Comptes Rendus*, 1882, xcv., 410). It therefore seemed probable that separation of this alum from alcoholic solution might furnish a convenient means for the recovery of gallium from such residues as those above mentioned. The development of such a method made necessary the determination of the approximate solubility of ammonium gallium alum and of the corresponding cæsium alum

would doubtless be even less soluble a sample of that compound was prepared and its solubility was determined.

A sample of each of these two alums was placed in a small bottle, an amount of water insufficient to completely dissolve the sample was added to each, and the mixture held at 25° in the thermostat for six hours. The gallium present in weighed amounts of the saturated supernatant solution was then determined.

The solubilities were then determined for each of the alums, using first 50 per cent alcohol and next 70 per cent alcohol. After the mixture had been held in the thermostat for 25° for six hours, 40 cc. of the supernatant liquid was pipetted off in each case and was evaporated to dryness. Each residue was then heated for two hours at 150° and was weighed as the mixture of the anhydrous sulphate of gallium with ammonium sulphate or with cæsium sulphate. The solubilities of each of the alums in a mixture of 35 cc. of water, 50 cc. of absolute ethyl alcohol, and 15 cc. concentrated hydrochloric acid was then determined. The gallium in samples of 40 cc. of the saturated supernatant solution was precipitated by the sodium sulphite method. The results of these various determinations follow :—

Solubility of Ammonium Gallium Sulphate Alum.

1. In water.

Weight of saturated solutions taken (grms.)	1·0248	0·7010
Weight of Ga_2O_3 found (grm.)	0·0463	0·0309

The average of these values is 0·0446 grm. of Ga_2O_3 per grm. of solution. One part of the salt therefore dissolves in 3·24 parts of water at 25°, and 100 cc. of the solution contains 30·84 grms. of the alum.

2. In 50 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0·0049 grm., which corresponds to 0·0411 grm. of Ga_2O_3 or 0·2170 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 4600 parts of 50 per cent alcohol at 25°, and 100 cc. of the solution contains 0·0217 grm. of the alum.

3. In 70 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0·0020 grm., which corresponds to 0·0166 grm. of Ga_2O_3 or 0·0875 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 11,400 parts of 70 per cent alcohol at 25°, and 100 cc. of the solution contains 0·00875 grm. of the alum.

4. In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, 15 cc. of concentrated sulphuric acid. 40 cc. of the saturated solution of the alum yielded 0·0122 grm, of Ga_2O_3, which corresponds to 0·305 grm. of Ga_2O_3 or 1·613 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 620 cc. of this solution at 25°, and 100 cc. of the solution contains 0·1613 grm. of the alum.

The Solubility of Cæsium Gallium Sulphate Alum.

1. In water.

Weight of saturated solution taken (grms.)	2·0812	1·7305
Weight of Ga_2O_3 found (grm.)	0·0048	0·0040

The average of these values is 0·0023 grm. of Ga_2O_3 per grm. of solution. One part of the salt therefore dissolves in 66·2 cc. of water at 25°, and 100 cc. of the solution contains 1·51 grms. of the alum.

2. In 50 per cent alcohol. 40 cc. of the saturated solution gave a residue that weighed 0·0010 grm., which corresponds to 0·0059 grm. of Ga_2O_3 or 0·0387 grm. of cæsium gallium alum per litre of solution. One part of the salt therefore dissolves 25,800 parts of 50 per cent alcohol at 25°, and 100 cc. of the solution contains 0·00387 grm. of the alum.

3. In 70 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0·0009 grm., which corresponds to 0·0054 grm. of Ga_2O_3 or 0·0356 grm. of cæsium gallium alum per litre of solution. One part of the salt therefore dissolves in 28,000 parts of 70 per cent alcohol at 25°, and 100 cc. of the solution contains 0·00356 grm. of the alum.

4. In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, and 15 cc. of concentrated sulphuric acid. 40 cc. of the saturated solution of the alum yielded 0·0014 grm. of Ga_2O_3, which corresponds to 0·0350 grm. of Ga_2O_3 or 0·228 grm. of cæsium gallium alum per litre of solution. One part of the salt therefore dissolves in 4380 parts of this solution at 25°, and 100 cc. of the solution contains 0·0228 grm. of the alum.

Summary.

1. The spark spectra and the arc spectra of gallium, indium, and zinc have been studied, and the delicacy of the spectroscopic detection of gallium and indium alone and in the presence of each other ascertained. Gallium chloride prepared by double distillation is found to contain less than 0·005 per cent of either indium or zinc.

2. The purification of gallium by fractional electrolysis, and the preparation of pure gallium chloride by distillation are described.

3. Methods for the determination of gallium alone and of gallium, indium, zinc, and aluminium in the presence of one another have been developed.

4. Two new salts of gallium, gallium selenate and cæsium gallium selenate alum, have been prepared. The solubilities of ammonium gallium sulphate alum and of cæsium gallium sulphate alum in water, in 50 per cent alcohol and in 70 per cent alcohol, have been measured.

MEASUREMENT OF THE THICKNESS OF FILM FORMED ON GLASS AND SAND.*

By EARL PETTIJOHN.

(Concluded from p. 296).

Experimental. — In order to obtain the relationship between surface and amount of liquid to produce sticking, a series of determinations was conducted using the glass pearls, water being used as the titrating liquid. Under these conditions the only variables were those of the solid, including the nature of the surface, the size and the specific gravity of the pearls. For samples from the same source no difference in the nature of the surface was to be expected.

During the whole of this work an attempt was made to find other material suitable for titration and of known surface. Results with this material would permit conclusions to be drawn regarding the capacity of different surfaces to hold liquid films and would thus show the effect of the other variants. No other material was found that could be used in this way.

Reproducibility of Results.—The apparatus as used was subject to some error due to the fact that the quantity of liquid added could only be controlled by opening the lower stopcock of the weight burette. To give an idea of the accuracy obtainable with this apparatus, a series of results obtained with each of two liquids is included. The remaining liquids gave results correspondingly accurate (see Table A).

The per cent error introduced depended principally on the amount of surface titrated or on the amount of liquid added, the greatest variation amounting to from 0·004 to 0·006 grm. of liquid.

The results obtained and the calculations of film thickness are given in Table II.

Discussion of Results.—The liquid required for a titration may be used to form a uniform film of liquid over the surface of the pearls up to the thickness at which flow

* From the *Journal of the American Chemical Society* xli., No. 4.

TABLE II.—*Titration Values Using Water.*

Sample. Pearls.	Diameter in cm.	Surface sq. cm./grm.	Sp. gr.	Weight.	Titration liquid per grm.	Film thickness.
No. 1.	0·1367	14·67	3·101	0·003988	0·000190	0·0000129
No. 3.	0·1180	17·09	3·090	0·002626	0·000218	0·0000128
No. 5.	0·0808	24·03	3·079	0·000853	0·000303	0·0000126
No. 7.	0·0542	35·46	3·125	0·000261	0·000402	0·0000113
No. 8.	0·0410	46·40	3·069	0·000121	0·000595	0·0000128
No. 9.	0·0540	44·93	2·505	0·000206	0·000297	0·0000066
No. 10.	0·0460	53·14	2·496	0·000122	0·000375	0·0000070
			Sands.			
Ottawa	0·0790	28·58	2·656	0·000686	0·000374	0·0000130
10-mesh	0·0494	46·00	2·643	0·000168	0·001310	0·0000285
20-mesh	0·0430	52·28	2·646	0·000110	0·001120	0·0000214
40-mesh	0·0280	81·90	2·650	0·000030	0·001100	0·0000135
60-mesh	0·0170	129·57	2·666	0·000007	0·001480	0·0000114

TABLE III.—*Titration Values for Sands and Pearls with Organic Liquids.*

Sands.

Liquids.	10-mesh.	20-mesh.	40 mesh.	60-mesh.	Ottawa.
Nitrobenzene	0·00136	0·00117	0·00109	0·00148	0·00039
Water	0·00133	0·00108	0·00112	0·00151	0·00037
Aniline	0·00122	0·00107	0·00109	0·00148	0·00039
Dimethylaniline	0·00131	0·00108	0·00107	0·00155	0·00039
Phenyliodide	0·00126	0·00112	0·00112	0·00149	0·00039
Toluol	0·00134	0·00116	0·00110	0·00146	0·00038
Turpentine	0·00131	0·00116	0·00108	0·00142	0·00039
Pyridine	—	—	0·00109	—	—

Pearls.

Liquids.	No. 1.	No. 3.	No. 5.	No. 8.	No. 9.	No. 10
Nitrobenzene	0·00018	0·00020	0·00030	0·00056	0·00027	0·00040
Water	0·00019	0·00022	0·00030	0·00059	0·00030	0·00037
Aniline	—	—	—	0·00055	0·00023	0·00039
Dimethylanilne	0·00017	0·00022	0·00032	0·00059	0·00029	0·00045
Phenyliodide..	0·00018	—	—	0·00059	0·00030	0·00039
Toluol	—	0·00021	—	0·00053	0·00031	0·00038

would occur. If this is the case a negligible amount of liquid would be required actually to support the grains, this amount being added after the uniform film had been added, and "sticking" would result from a concentration of this added amount at the contact surface of flask and pearl through the action of capillary forces.

TABLE A.

Liquid.	Water.	Nitrobenzene.
Sample	200 grms. pearls No. 8.	200 grms. pearls No. 3.
Weight of liquid, grms. ..	0·119	0·040
	0·119	0·041
	0·117	0·039
	0·116	0·042
	0·120	0·042
	0·121	0·038
	0·116	
	0·118	
Average	0·118	0·040
Greatest variation from average	0·003 = 2·5 p.c.	= 5 p.c.
Variation between highest and lowest values.. ..	4·2 p.c.	10 p.c.

On the other hand, the whole amount of liquid required may be necessary to support the pearls through the action of surface tension. In this case no film would form, but all of the liquid added would concentrate at the contact surface, and "sticking" would occur as soon as the surface tension was sufficient to support the pearl.

In order to determine which of these two hypotheses held or whether the amount used in titrating was the resultant of both effects, some calculations were made of the amount of liquid necessary to support a single grain.

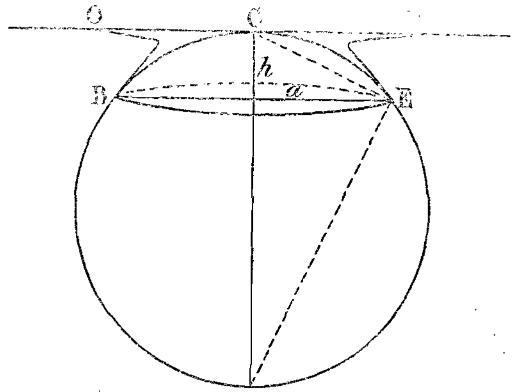


FIG. 2.

Fig. 2 will explain the letters used and the method of calculation followed.

Consider a pearl weighing 0·0001 grm., held to the surface of the flask by surface tension. The liquid holding the pearl may be considered as occupying a volume represented in section by (OBCED), the lowest level of this volume being the circumference of a circle whose radius

would doubtless be even less soluble a sample of that compound was prepared and its solubility was determined.

A sample of each of these two alums was placed in a small bottle, an amount of water insufficient to completely dissolve the sample was added to each, and the mixture held at 25° in the thermostat for six hours. The gallium present in weighed amounts of the saturated supernatant solution was then determined.

The solubilities were then determined for each of the alums, using first 50 per cent alcohol and next 70 per cent alcohol. After the mixture had been held in the thermostat at 25° for six hours, 40 cc. of the supernatant liquid was pipetted off in each case and was evaporated to dryness. Each residue was then heated for two hours at 150° and was weighed as the mixture of the anhydrous sulphate of gallium with ammonium sulphate or with cæsium sulphate. The solubilities of each of the alums in a mixture of 35 cc. of water, 50 cc. of absolute ethyl alcohol, and 15 cc. concentrated hydrochloric acid was then determined. The gallium in samples of 40 cc. of the saturated supernatant solution was precipitated by the sodium sulphite method. The results of these various determinations follow :—

Solubility of Ammonium Gallium Sulphate Alum.

1. In water.

Weight of saturated solutions taken (grms.)	1·0248	0·7010
Weight of Ga_2O_3 found (grm.)	0·0463	0·0309

The average of these values is 0·0446 grm. of Ga_2O_3 per grm. of solution. One part of the salt therefore dissolves in 3·24 parts of water at 25°, and 100 cc. of the solution contains 30·84 grms. of the alum.

2. In 50 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0·0049 grm., which corresponds to 0·0411 grm. of Ga_2O_3 or 0·2170 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 4600 parts of 50 per cent alcohol at 25°, and 100 cc. of the solution contains 0·0217 grm. of the alum.

3. In 70 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0·0020 grm., which corresponds to 0·0166 grm. of Ga_2O_3 or 0·0875 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 11,400 parts of 70 per cent alcohol at 25°, and 100 cc. of the solution contains 0·00875 grm. of the alum.

4. In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, 15 cc. of concentrated sulphuric acid. 40 cc. of the saturated solution of the alum yielded 0·0122 grm, of Ga_2O_3, which corresponds to 0·305 grm. of Ga_2O_3 or 1·613 grm. of ammonium gallium alum per litre of solution. One part of the salt therefore dissolves in 620 cc. of this solution at 25°, and 100 cc. of the solution contains 0·1613 grm. of the alum.

The Solubility of Cæsium Gallium Sulphate Alum.

1. In water.

Weight of saturated solution taken (grms.)	2·0812	1·7305
Weight of Ga_2O_3 found (grm.)	0·0048	0·0040

The average of these values is 0·0023 grm. of Ga_2O_3 per grm. of solution. One part of the salt therefore dissolves in 66·2 cc. of water at 25°, and 100 cc. of the solution contains 1·51 grms. of the alum.

2. In 50 per cent alcohol. 40 cc. of the saturated solution gave a residue that weighed 0·0010 grm., which corresponds to 0·0059 grm. of Ga_2O_3 or 0·0387 grm. of cæsium gallium alum per litre of solution. One part of the salt therefore dissolves 25,800 parts of 50 per cent alcohol at 25°, and 100 cc. of the solution contains 0·00387 grm. of the alum.

3. In 70 per cent alcohol. 40 cc. of the saturated solution of the alum gave a residue that weighed 0·0009 grm., which corresponds to 0·0054 grm. of Ga_2O_3 or 0·0356 grm. of cæsium gallium alum per litre of solution. One part of the salt therefore dissolves in 28,000 parts of 70 per cent alcohol at 25°, and 100 cc. of the solution contains 0·00356 grm. of the alum.

4. In a solution containing 35 cc. of water, 50 cc. of absolute alcohol, and 15 cc. of concentrated sulphuric acid. 40 cc. of the saturated solution of the alum yielded 0·0014 grm. of Ga_2O_3, which corresponds to 0·0350 grm. of Ga_2O_3 or 0·228 grm. of cæsium gallium alum per litre of solution. One part of the salt therefore dissolves in 4380 parts of this solution at 25°, and 100 cc. of the solution contains 0·0228 grm. of the alum.

Summary.

1. The spark spectra and the arc spectra of gallium, indium, and zinc have been studied, and the delicacy of the spectroscopic detection of gallium and indium alone and in the presence of each other ascertained. Gallium chloride prepared by double distillation is found to contain less than 0·005 per cent of either indium or zinc.

2. The purification of gallium by fractional electrolysis, and the preparation of pure gallium chloride by distillation are described.

3. Methods for the determination of gallium alone and of gallium, indium, zinc, and aluminium in the presence of one another have been developed.

4. Two new salts of gallium, gallium selenate and cæsium gallium selenate alum, have been prepared. The solubilities of ammonium gallium sulphate alum and of cæsium gallium sulphate alum in water, in 50 per cent alcohol and in 70 per cent alcohol, have been measured.

MEASUREMENT OF THE THICKNESS OF FILM FORMED ON GLASS AND SAND.*

By EARL PETTIJOHN.

(Concluded from p. 296).

Experimental. — In order to obtain the relationship between surface and amount of liquid to produce sticking, a series of determinations was conducted using the glass pearls, water being used as the titrating liquid. Under these conditions the only variables were those of the solid, including the nature of the surface, the size and the specific gravity of the pearls. For samples from the same source no difference in the nature of the surface was to be expected.

During the whole of this work an attempt was made to find other material suitable for titration and of known surface. Results with this material would permit conclusions to be drawn regarding the capacity of different surfaces to hold liquid films and would thus show the effect of the other variants. No other material was found that could be used in this way.

Reproducibility of Results.—The apparatus as used was subject to some error due to the fact that the quantity of liquid added could only be controlled by opening the lower stopcock of the weight burette. To give an idea of the accuracy obtainable with this apparatus, a series of results obtained with each of two liquids is included. The remaining liquids gave results correspondingly accurate (see Table A).

The per cent error introduced depended principally on the amount of surface titrated or on the amount of liquid added, the greatest variation amounting to from 0·004 to 0·006 grm. of liquid.

The results obtained and the calculations of film thickness are given in Table II.

Discussion of Results.—The liquid required for a titration may be used to form a uniform film of liquid over the surface of the pearls up to the thickness at which flow

* From the *Journal of the American Chemical Society* xli., No. 4.

TABLE II.—*Titration Values Using Water.*

Sample. Pearls.	Diameter in cm.	Surface sq. cm./grm.	Sp. gr.	Weight.	Titration liquid per grm.	Film thickness.
No. 1.	0·1367	14·67	3·101	0·003988	0·000190	0·0000129
No. 3.	0·1180	17·09	3·090	0·002626	0·000218	0·0000128
No. 5.	0·0808	24·03	3·079	0·000853	0·000303	0·0000126
No. 7.	0·0542	35·46	3·125	0·000261	0·000402	0·0000113
No. 8.	0·0410	46·40	3·069	0·000121	0·000595	0·0000128
No. 9.	0·0540	44·93	2·505	0·000206	0·000297	0·0000066
No. 10.	0·0460	53·14	2·496	0·000122	0·000375	0·0000070
			Sands.			
Ottawa	0·0790	28·58	2·656	0·000686	0·000374	0·0000130
10-mesh	0·0494	46·00	2·643	0·000168	0·001310	0·0000285
20-mesh	0·0430	52·28	2·646	0·000110	0·001120	0·0000214
40-mesh	0·0280	81·90	2·650	0·000030	0·001100	0·0000135
60-mesh	0·0170	129·57	2·666	0·000007	0·001480	0·0000114

TABLE III.—*Titration Values for Sands and Pearls with Organic Liquids.*

Sands.

Liquids.	10-mesh.	20-mesh.	40 mesh.	60-mesh.	Ottawa.
Nitrobenzene	0·00136	0·00117	0·00109	0·00148	0·00039
Water	0·00133	0·00108	0·00112	0·00151	0·00037
Aniline	0·00122	0·00107	0·00109	0·00148	0·00039
Dimethylaniline	0·00131	0·00108	0·00107	0·00155	0·00039
Phenyliodide	0·00126	0·00112	0·00112	0·00149	0·00039
Toluol	0·00134	0·00116	0·00110	0·00146	0·00038
Turpentine	0·00131	0·00116	0·00108	0·00142	0·00039
Pyridine	—	—	0·00109	—	—

Pearls.

Liquids.	No. 1.	No. 3.	No. 5.	No. 8.	No. 9.	No. 10
Nitrobenzene	0·00018	0·00020	0·00030	0·00056	0·00027	0·00040
Water	0·00019	0·00022	0·00030	0·00059	0·00030	0·00037
Aniline	—	—	—	0·00055	0·00023	0·00039
Dimethylanilne	0·00017	0·00022	0·00032	0·00059	0·00029	0·00045
Phenyliodide..	0·00018	—	—	0·00059	0·00030	0·00039
Toluol	—	0·00021	—	0·00053	0·00031	0·00038

would occur. If this is the case a negligible amount of liquid would be required actually to support the grains, this amount being added after the uniform film had been added, and "sticking" would result from a concentration of this added amount at the contact surface of flask and pearl through the action of capillary forces.

TABLE A.

Liquid.	Water.	Nitrobenzene.
Sample	200 grms. pearls No. 8.	200 grms. pearls No. 3.
Weight of liquid, grms. ..	0·119	0·040
	0·119	0·041
	0·117	0·039
	0·116	0·042
	0·120	0·042
	0·121	0·038
	0·116	
	0·118	
Average	0·118	0·040
Greatest variation from average	0·003 = 2·5 p.c.	= 5 p.c.
Variation between highest and lowest values.. ..	4·2 p.c.	10 p.c.

On the other hand, the whole amount of liquid required may be necessary to support the pearls through the action of surface tension. In this case no film would form, but all of the liquid added would concentrate at the contact surface, and "sticking" would occur as soon as the surface tension was sufficient to support the pearl.

In order to determine which of these two hypotheses held or whether the amount used in titrating was the resultant of both effects, some calculations were made of the amount of liquid necessary to support a single grain.

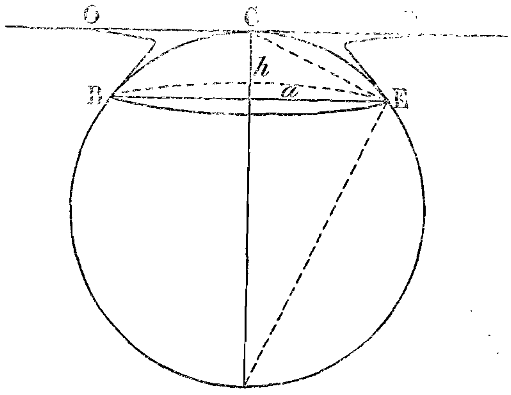


FIG. 2.

Fig. 2 will explain the letters used and the method of calculation followed.

Consider a pearl weighing 0·0001 grm., held to the surface of the flask by surface tension. The liquid holding the pearl may be considered as occupying a volume represented in section by (OBCED), the lowest level of this volume being the circumference of a circle whose radius

is a. Surface tension may be considered as acting along this circumference. If the surface tension and the weight supported by it are known, the length of the circumference required to support the pearl is given 0·0001/sur. ten. Substituting actual values and placing the quotient equal to the circumference of a circle enables one to calculate the value of a in the same units as are used for expressing the surface tension (cm.). Having the value of a, the value of h (thickness of liquid acting) may be calculated, since by geometry—

$$h : a :: a : (R - h),$$

and all of the terms except h are known.

Knowing both a and h, the volume of liquid holding the pearl can be estimated. It was assumed that the volume of liquid necessary to support the pearl would be that required to half fill the volume represented on the figure by (OBED). This is believed to be in excess of the actual amount needed. Calculating this value for the smallest pearl used, one weighing 0·00312 grm. gave 0·0837 cc. per grm. of pearls. Calculating the same value for pearls No. 1, the heaviest pearls used, gave 0·058 cc. per grm. of pearls. These amounts are negligible when the amounts required for a titration are considered. This shows clearly that although the end-point is marked by the appearance of "sticking," which is a surface-tension effect, surface tension itself cannot account for the liquid required for a titration.

The amount of liquid required is directly proportional to the surface, and the film thickness is uniform for the same kind of glass.

As to the actual thickness of film found, it is of the same order as that found by earlier investigators who worked with the vapour phase of water in forming the film. The results are higher than those of all except Parks. It does not seem probable, in view of the results obtained, that there is any difference in the nature of the film itself, whether water in the vapour phase or water in the liquid phase is used to form the film. It also seems probable that what actually takes place on the surface of the grain is a condensation of water vapour. In the titrations in which water was used to form the film it was found that the titrated sample on air drying would again take up the same amount of liquid. It is difficult to see how this could take place repeatedly if a chemical reaction was involved in holding the liquid.

The results obtained with samples No. 9 and No. 10 are only about half as large as those obtained with the rest of the samples. This can only be due to a different surface capacity for holding liquid. The results are close to those obtained by Katz with ornithite, and by Ihmori with glass globes.

Ottawa sand gives the same value for film thickness that the larger series of pearls does. It seems probable that this is a chance agreement, since the surface of the sand differed considerably from that of the pearls both in hardness and in texture.

As a whole, the results indicate that there are two factors which influence the amount of liquid necessary to form the maximum thickness of film. The first factor is the amount of surface, the actual area that the film must cover. The second is the nature of the surface itself, its capacity to hold a film.

Not a great deal is known regarding the variants which determine the capacity factor of a surface. It is probably related to the free energy present in the atoms of the surface layers.

The work up to this point indicated that the film thickness should be independent of the liquid used, providing the liquid is not too viscous to spread readily. It also indicated the desirability of applying the titration method to the determination of the surface of irregular particles like sand grains.

For the purpose of obtaining surface values for the meshed sands complete titrations for each of these samples with water and with each of the organic liquids was carried out. An attempt was made also to titrate finer sands, 100-mesh, 150-mesh, 200-mesh. These, however, would not permit of an even distribution of the liquid over the surface, and no satisfactory titrations were obtainable.

To determine whether the same thickness of film would be found with a different liquid, titrations were carried out first with the pearls and then with the sands, making use of the organic liquids. The determinations with the pearls were not completed when they were found to check closely for the first liquids used, but those on the sands were completed for all of the liquids.

The organic liquids used were chosen so that the specific gravity, volatility, surface tension, &c., varied.

The results obtained from these two series of titrations are given in Table III., and will be discussed together.

Discussion of Results.—The results show that the thickness of the film is independent of the kind of liquid used for titrating, and that the sand titrations can be checked with as good an accuracy as titrations of pearls. Occasional results vary, but the uniformity for the whole series is pronounced. This proves definitely that the surface tension of the liquid has no effect on the amount of liquid required for a titration. The surface tension of water is much greater than that of the other liquids, but the volume required per grm. is the same. This could not be true if the surface tension influenced the amount of liquid required to produce "sticking."

It also proves that there is no chemical reaction in the ordinary sense of the term when a film of water forms on glass. While it might be possible to imagine such an effect between water and glass, it is obviously impossible to do so with the rest of the liquids of the series. In addition to this the calculated film thickness for different sizes of pearls is found to be the same, showing that the volume for titration varies with the surface.

The definite conclusion can be drawn that these films are not due to the formation of a chemical compound, but that they are held by the free surface energy of the solid. It seems certain that the same force holds a thinner film.

While these films are formed by the addition of liquid to the solid, the inference is that the same conclusion may be drawn for a film formed from the vapour phase. This inference is supported by the fact that the values obtained for the film thickness when formed from the vapour phase are only very slightly lower than those formed by the addition of liquid. It seems probable that a liquid film forms in both cases, but that with the unsaturated vapour phase it never becomes thick enough to show as a normal liquid on the surface of the solid, while when liquid is used the formation of free liquid marks the end of the titration and indicates the thickest film that can form without free liquid being present.

In titrating sands a simple relationship such as was found for the pearl samples does not exist between titrated amount and calculated surface. This is partly due to error in calculating the surface, on the assumption that the grains are spherical, and partly to the fact that extra liquid is required to fill the etchings in the surface. However, if relative effective surfaces are sought they may be expected to be proportional to the titration values, since there is no application of the surface which would not involve the etchings and so produce results which would be proportional to those obtained by the titration method.

Summary.

This paper describes a new method of obtaining the thickness of the maximum film which can form on a surface without free liquid being present. Evidence is presented to show that the liquid forming the film does not combine chemically with the solid. The method has been applied to sand and to glass, and films have been formed with water and with several organic liquids. The film thickness is found to be independent of the liquid used and of the size of the solid particle. The method gives

accurate values for the effective surface of sand particles, providing that surfaces of the same kind are compared.

In conclusion I wish to express my indebtedness to Prof. I. H. Derby for his advice and suggestions in the preparation of this paper.

LEAD IN PHARMACEUTICAL ZINC OXIDE.

By W. D. COLLINS and W. F. CLARKE.

Soon after the outbreak of the present war, difficulty was experienced in obtaining pharmaceutical zinc oxide which would meet the requirements of the United States Pharmacopœia. When the matter was first considered, the statement was made that zinc oxide of the required purity was very easy to obtain. It was even stated that material bought for use as a pigment in painting might be more nearly free from lead than a certain sample of pharmaceutical zinc oxide which contained about 0·2 per cent of lead.

Mr. C. L. Black, of the Philadelphia Station of the Bureau of Chemistry, reported in May, 1917, that analysis of such samples of zinc oxide as could be procured on the market at that time indicated that practically all the zinc oxide obtainable contained more lead than was permitted by the U.S.P. test. Some manufacturers at this time stated on the labels that the zinc oxide sold by them contained heavy metals slightly in excess of the U.S.P. limit. Prof. C. H. La Wall published an article calling attention to this matter, and made the suggestion that all samples of pharmaceutical zinc oxide should be tested for lead. (*Am. Journ. Pharm.*, 1917, lxxxix., 353. In a later article (*Ibid.*, 1918, xc., 499) Prof. Le Wall notes that U.S.P. zinc oxide is now on the market. He proposes tests for lead which will detect 0·03 per cent PbO in zinc oxide, while the present U.S.P. test under the best conditions will detect 0·05 per cent).

In order to learn whether it would be possible to obtain zinc oxide reasonably free from lead, samples were obtained on the market and from manufacturers, and the question was taken up with the U.S. Geological Survey, and with manufacturers of zinc oxide. It was learned from Mr. C. E Siebenthal, of the U.S. Geological Survey, that one company producing zinc in the United States owned a mine which contained no lead minerals, and therefore should be able to produce zinc oxide free from lead. It would seem probable that zinc oxide made from electrolytic zinc should be free from lead. It was learned from manufacturers that zinc oxide was being made according to both of these principles, and that the products contained much less lead than the amount necessary to respond to the U.S.P. test for heavy metals.

Test for Lead in Zinc Oxide by the U.S.P. Test for Heavy Metals.

In order to determine the sensitiveness of the U.S.P. test for lead in zinc oxide two series of experiments were conducted entirely independently in order to establish the limits of sensitiveness. Different quantities of lead from a solution of lead nitrate were made up with zinc oxide and hydrochloric acid so as to give the concentrations of zinc and acid prescribed by the U.S.P. for the test for heavy metals. In one series of tests (W.F.C.) the hydrogen sulphide used was made according to the directions of the Pharmacopœia. In the other series of tests (W.D.C.) the hydrogen sulphide used was prepared in the ordinary manner by the use of hydrochloric acid and ferrous sulphide and the gas was washed through water. No difference could be detected in the results by the two methods.

It was found that a sample of zinc oxide might contain as much as 0·05 per cent lead and fail to respond to the test for heavy metals. In some cases the test would be obtained and in others it would fail. When the sample contained as much as 0·1 per cent a positive test was always obtained, and with any amount greater than 0·05 per cent there was rarely any doubt about the response to the test.

Samples.

A number of samples of zinc oxide were purchased at various drug stores. Some samples were furnished by manufacturers and others were obtained from dealers through the regular purchasing office of the Bureau.

Table I.—*Zinc Oxide.*

Sample No.	Received.	Dealer.	Producer or manufacturer.	Lead. per cent.	U.S.P. test.
117 (*a*)	1-13-17	A	?	0·25	+
118 (*a*)	1-16-17	B	C	0·036	0
119 (*a*)	1-16-17	A	?	0·25	+
133 (*a*)	8-4-17	D	E	0·19	—
134 (*a*)	8-4-17	F	G	0·19	+
137 (*a*)	8-6-17	B	C	0·26	+
130 (*b*)	1915	H	H	0·041	0
148 (*c*)	9-27-17	I	I	0·006	0
158 (*d*)	11-28-17	I	I	0·004	0
159 (*d*)	11-29-17	I	I	0·008	0
155 (*e*)	11-5-17	C	K	0·013	0
178 (*e*)	2-1-18	H	I	0·004	0
187 (*e*)	2-4-18	L	I	0·008	0
			Metallic Zinc.		
149 (*f*)	1914	—	M	0·026	—
145 (*g*)	1917	N	M probably	0·094	—
146 (*h*)	9-26-17	—	K	0·012	—
			Pigment Zinc Oxide.		
135 (*i*)	8-4-17	O	—	0·13	Trace
136	8-4-17	P	—	53·2	Heavy

(*a*) Purchased at local drug store.
(*b*) From Bureau stock of reagents.
(*c*) Show sample from office of manufacturer.
(*d*) Sample sent by manufacturer.
(*e*) Purchased by Bureau Supply Office.
(*f*) Analysis on label, lead 0·01 per cent.
(*g*) Analysis on label, lead none.
(*h*) Sample furnished by manufacturer.
(*i*) About 22 per cent barium sulphate.

Samples of zinc oxide were also purchased at two paint stores. A few samples of metallic zinc were examined for their content of lead.

Method of Analysis.

Lead was determined by the well known method of separating as sulphate and weighing as chromate. From 5 to 40 grms. of zinc oxide or zinc were dissolved in water and sulphuric acid, with a slight excess of acid. The volume was usually about 100 cc. for 10 grms. of zinc oxide. Alcohol (95 per cent) was added in quantity just short of that necessary to start precipitation of the zinc sulphate, usually making about one-third of the final volume. The solution was allowed to stand overnight; the lead sulphate was filtered off on asbestos, washed with 50 per cent alcohol, and dissolved in ammonium acetate. The lead was reprecipitated as chromate, after acidifying with acetic acid, by adding potassium dichromate solution. After standing overnight the lead chromate was filtered on asbestos in a weighed Gooch crucible, dried to constant weight at 110°, and weighed. The accompanying table gives descriptions of the samples and the results obtained for lead, and also the results of testing according to the United States Pharmacopæia.

Summary.

For a short time after the beginning of the war it was not possible to procure zinc oxide of the U.S.P. standard produced in the United States.

The U.S.P. test for heavy metals will not detect less than 0·05 per cent of lead in zinc oxide.

It is possible at the present time to obtain zinc oxide which, with respect to the presence of lead, is of much higher quality than is called for by the requirements of the U.S.P. — *Journal of Industrial and Engineering Chemistry*, ii., No. 2.

BOARD OF TRADE ANNOUNCEMENTS.

The Board of Trade are in receipt of information from the Foreign Office that the Danish Government have now given a general guarantee, which has been accepted by the Associated Governments, that goods imported into that country will not be re-exported to enemy countries. They announce therefore that, except for goods on Lists A or B, all restrictions on export to Denmark, whether by freight or by parcel post, have been removed.

Exporters should, however, satisfy themselves that the goods are not subject to any Danish import prohibition.

Applications for licences to export goods on Lists A or B should continue to be made to the Export Licence Department (4, Central Buildings, Westminster, S.W. 1), but no certificates from the Danish Associations need be produced.

Import of Dyestuffs.

By the Proclamation of February 24, 1919, the importation into the United Kingdom of the following products was prohibited except under licence, viz. :—

All derivatives of coal-tar generally known as intermediate products capable of being used or adapted for use as dyestuffs, or of being modified or further manufactured into dyestuffs.

All direct cotton colours, all union colours, all acid wool colours, all chrome and mordant colours, all alizarine colours, all basic colours, all sulphide colours, all vat colours (including synthetic indigo), all oil, spirit, and wax colours, all lake colours, and any other synthetic colours, dyes, stains, colour acids, colour bases, colour lakes, leuco acids, leuco bases, whether in paste, powder, solution, or any other form.

At the same time, in accordance with the arrangements outlined in a White Paper issued some months ago (Cd. 9194) setting out the Government scheme for affording State assistance to the dye-making industry, a special Committee, known as the Trade and Licensing Sub-Committee, was established with offices at Danlee Buildings, 53, Spring Gardens, Manchester, in order to determine the kinds and quantities of the dyestuffs which were to be licenced for import and generally to deal with all questions relating to such importation.

This Sub-Committee consists of Dr. A. Ree and Mr. J. Turner (representing the dye manufacturing industry) and Mr. W. E. Kay and Mr. Thorp Whitaker (representing the dye using industry), with Mr. W. Graham of the Board of Trade as Secretary.

In order that there should be no undue delay in dealing with applications to import dyestuffs during the first few weeks whilst the necessary organisation was being set up, the Committee issued a General Licence permitting the importation of all dyestuffs of *bona-fide* American, French, or Swiss origin, but this concession was withdrawn on April 9, and since that date licences have been necessary for the import of all consignments of dyestuffs coming into this country whatever their origin.

Whilst the regulation of the import of dyestuffs was primarily necessitated in order to prevent the free access of German materials to this market it was felt that some measure of control was desirable over all imports if the scheme was to be thoroughly effective. It was therefore decided that a Central Importing Agency should be established under the direct control of the Committee through which all imports of dyestuffs must pass at some stage. As soon as the Committee are in a position to consider applications for the import of German dyestuffs, which will not be until after the withdrawal of the Trading with the Enemy Regulations, the Central Importing Agency will be the medium through which supplies are made available to consumers. Except in the case of German dyes, the Agency will now undertake if desired the purchase of dyestuffs abroad on behalf of consumers, but where it is desired to make purchases direct or through recognised merchants the goods will merely require to be consigned to the Agency for the account of the particular consignee and the shipping documents made out accordingly. For its services the Agency will charge a commission of 1 per cent on the invoice value of the goods with a minimum charge of 5s., but this charge will not, of course, include any incidental expenses such as freight, insurance, storage, &c., which must naturally be additional and borne by the importer. The Offices of the Central Importing Agency for the time being are at 21, Spring Gardens, Manchester.

Any firms desiring further information on the subject or wishing to make application for an import licence are advised to communicate direct with the Secretary of the Licensing Sub-Committee, at the address already given (53, Spring Gardens, Manchester).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 5, 1919.

Sir J. J. Thomson, O.M., President, in the Chair.

The following papers were read :—

"*The Relation between the Refractivity and Density of Carbon Dioxide.*" By P. Phillips, D.Sc.

"*On the Colours of the Striæ in Mica, and the Radiation from Laminar Diffracting Boundaries.*" By P. N. Ghosh.

(*a*) The striæ are shown by an examination of the Haidinger's rings in mica (and otherwise) to be the boundaries between parts having slightly different thicknesses.

(*b*) The colour of any stria as seen in the Foucault test is complementary to the colour of the central fringe in the laminary diffraction-pattern produced by it.

(*c*) The colours are altered by holding the mica obliquely, or by immersing it in a cell containing liquid.

(*d*) The luminosity of a stria in the Foucault test is approximately a maximum when the phases of the wave-front, after passing through the plate on the two sides of the stria, are opposite, and practically zero when the phases are identical.

(*e*) Attempts to reproduce the phenomenon by etching glass plates with dilute hydrofluoric acid were not very successful, owing, apparently, to a want of sufficient sharpness in the boundary thus produced. This is indicated by the fact that such a plate shows distinct *asymmetry* with reference to the direction of the incident light, both in the Foucault test and in laminar diffraction.

(*f*) The striæ in mica appear doubled (with a black line in the centre) when the light coming to a focus is screened in a symmetrical manner, instead of by a knife-edge, as in the Foucault test.

"*A Study of the Catalytic Actions at Solid Surfaces.*" By E. F. Armstrong, D.Sc., and T. P. Hilditch, D.Sc.

The rate of hydrogenation of a number of unsaturated fatty oils in presence of finely disseminated nickel has been studied and the results expressed in the form of curves. These are characterised by an initial linear segment followed by an abrupt change of direction to a segment of gentler slope, which is also linear at first, but

subsequently may exhibit considerable curvature. The point of inflexion is at a corresponding part of each curve. The two well-defined linear components of the curves correspond to the hydrogenation of glycerides more unsaturated than olein and to the hydrogenation of olein. The curves never approach the logarithmic type required for a unimolecular action.

The general aspect of the curves obtained for catalytic hydrogenation is markedly similar to those obtained in the case of enzymes, and they undoubtedly represent related phenomena. In each the catalyst (enzyme or reduced nickel) unites primarily with the organic compound about to undergo change (hydrolyte or unsaturated glyceride), the complex so formed being decomposed by the other component of the interaction (water or hydrogen). In each case, moreover, action takes place entirely at the surface of colloid particles, and activity of catalyst depends entirely on production of maximum surface and avoidance of impurities likely to destroy or dirty this surface.

It is considered that the interchanges take place in an electrolytic circuit in which the interacting substances are necessarily all comprised. Hydrogen and fatty oil are both to be thought of as coupled with nickel and interaction as brought about through inclusion in the system of the electrolyte required to establish a conducting circuit. Both hydrogen and fatty oil are to be regarded as having some affinity for the catalyst, and the rate of change is to be considered as determined by the rate at which the less active (hydrogen) enters into productive association with the catalyst.

OBITUARY

Sir BOVERTON REDWOOD.

The death of Sir Boverton Redwood, Bart., which took place on June 4 last, has deprived science and chemistry in particular of one of its most active workers.

Sir Boverton was born in April, 1846, and was therefore in his seventy-fourth year. Since the age of twenty-three, when he was appointed Secretary to the Petroleum Association, he has been an active and prominent man in the chemical world. He has served on many commissions connected with the Petroleum industry, and during the war gave much assistance to the Admiralty and other bodies.

His only son, Bernard Boverton, died in 1911, and his grandson, Thomas Boverton, born in 1906, succeeds to the baronetcy.

CORRESPONDENCE.

THE DISRUPTION OF THE NITROGEN ATOM.

To the Editor of the Chemical News.

Sir,—In the fourth paper of a series entitled "Collisions of α-Particles with Light Atoms," by Sir E. Rutherford (Papers I. to V., *Phil. Mag.*, June, 1919, pp. 537—587), there is an announcement that is somewhat sensational, and with your permission I will give a short account of the subject supplemented by the author's discussion of the results.

The nuclear theory of the atom indicates the possibility of impressing on the nuclei of light atoms a swift translatory motion by the impact of α-particles thereon, and in the case of bombarding hydrogen the H atom should acquire a velocity 1·6 times that of the α-particle when receiving therefrom a direct blow, whilst the energy acquired by the H atom should be 0·64 of the energy of the α-particle.

Prof. Marsden detected scintillations on a zinc sulphide screen, placed upon the range of the α-particles, due to the presence of high-speed H atoms when the α-particles were passed through gaseous hydrogen, the speed of the H atoms being considerably greater than that of the α-particles before impact; their range of projection under certain conditions is over 100 cm. in hydrogen, which is four times the movement of colliding α-particles in the same gas. Moreover, this range is in agreement with that calculated by Darwin from Bohr's theory of absorption of α-particles by matter. It was noted that the number of hydrogen scintillations was in all cases too great to be accounted for by the presence of hydrogen in the radio-active material used or at the source of the α-particles.

It was considered probable that besides the H atoms being driven in a definite direction, O and N atoms from the air were similarly given a high velocity, and it was found that these atoms produced scintillations on the screen, but in the absence of hydrogen scintillations appeared evidently due to hydrogen disrupted from the nitrogen by the force of the α-particle impacts. In regard to the experimental details given, with dried air the scintillations increased in number. While the scintillations were observed with air and oxygen no anomalous effect (see discussion below) was observed either with oxygen or carbon dioxide, and the comparative effect observed with chemically pure nitrogen indicates that the source of the effect, presumably due to the dismemberment of the nitrogen atom, arises from the nitrogen itself. The removal of dust from dry air did not appreciably reduce the effect. It was found that the scintillations varied with the air pressure in the vessel, as should be expected if they arise from the impacts of α-particles on the gases present. The presence of H atoms was indirectly confirmed by obtaining deflections in magnetic and electrostatic fields, but "in order to settle this question definitely it will probably be necessary to employ a solid nitrogen compound free from hydrogen as a source and use much stronger sources of α-rays."

It is of interest to note that for every 109 collisions with the hydrogen molecules only one α-particle passes close enough to the nucleus to give rise to a swift H atom.

After detailing a series of analytical experiments, touched upon above, which brought to light the apparent disruption or dismemberment of the nitrogen atom, Sir E. Rutherford concludes with the following discussion of the results:—

"From the results so far obtained it is difficult to avoid the conclusion that the long range atoms arising from collision of α-particles with nitrogen are not nitrogen atoms but probably atoms of hydrogen, or atoms of mass 2. If this be the case, we must conclude that the nitrogen atom is disintegrated under the intense forces developed in a close collision with a swift α-particle, and that the hydrogen atom which is liberated formed a constituent part of the nitrogen nucleus. We have drawn attention in Paper III. to the rather surprising observation that the range of the nitrogen atoms in air is about the same as the oxygen atoms, although we should expect a difference of about 19 per cent. If in collisions which give rise to swift nitrogen atoms, the hydrogen is at the same time disrupted, such a difference might be accounted for, for the energy is then shared between two systems. It is of interest to note, that while the majority of the light atoms, as is well known, have atomic weights represented by $4n$ or $4n+3$, where n is a whole number, nitrogen is the only atom which is expressed by $4n+2$. We should anticipate from radio-active data that the nitrogen nucleus consists of three helium nuclei each of atomic mass 4, and either two hydrogen nuclei or one of mass 2. If the H nuclei were outriders of the main system of mass 12, the number of close collisions with the bound H nuclei would be less than if the latter were free, for the α-particle in a collision comes under the combined field of the H nucleus and of the central mass. Under such conditions it is to be expected that the α-particle would only occasionally approach close

enough to the H nucleus to give it the maximum velocity, although in many cases it may give it sufficient energy to break its bond with the central mass. Such a point of view would explain why the number of swift H atoms from nitrogen is less than the corresponding number in free hydrogen and less also than the number of swift nitrogen atoms. The general results indicate that the H nuclei, which are released, are distant about twice the diameter of the electron (7×10^{-13} cm.) from the centre of the main atom. Without a knowledge of the laws of force at such small distances it is difficult to estimate the energy required to free the H nucleus or to calculate the maximum velocity that can be given to the escaping H atom. It is not to be expected, *à priori*, that the velocity or range of the H atom released from the nitrogen atom should be identical with that due to a collision in free hydrogen.

"Taking into account the great energy of the motion of the α-particle expelled from radium C, the close collision of such an α-particle with a light atom seems to be the most likely agency to promote the disruption of the latter; for the forces on the nuclei arising from such collisions appear to be greater than can be produced by any other agency at present available. Considering the enormous intensity of the forces brought into play, it is not so much a matter of surprise that the nitrogen atom should suffer distintegration as that the α-particle itself escapes disruption into its constituents."

Further developments will no doubt be awaited with interest.—I am, &c.,

F. H. LORING.

June, 1919.

NOTES.

GLUE.—A good sterile glue can be made by taking—Glue, 50; water, 50; *glycerin, 2; calcium chloride, 2;* thymol, 1. Melt and use hot.

THE Annual Report of the British Science Guild was presented by Sir Richard Gregory at a meeting held in the Goldsmiths' Hall on June 17. The chair was occupied by Lord Sydenham, who, at the conclusion of the Official business, gave an address on "Science and Labour Unrest." His Lordship suggested that the labour unrest, so manifest at the present time, is due to the triumphs of applied science, and also that science in its broadest aspect can provide the remedies and secure industrial peace. In a broad sketch commencing with Primitive man and the means he had to employ to enable him to maintain his existence, and ending with the present day mechanic, he showed how science by the recognition of principles and the invention of appliances to minimise manual exertion, has completely changed the character of labour, at all events of the educated European. The advantages and evils of trade unions were discussed, and the immediate need for grappling with the housing problem and the bettering of the conditions of the working classes was pointed out. In conclusion Lord Sydenham insists that every manual worker must honestly put forward his full effort within the agreed hours of labour, and there must be no idlers in this country. "There can be no room for them in the strenuous times which we must face. Knowledge we now have in abundance. Our future existence as a nation and an Empire depends upon whether we have wisdom in all classes. Science, which has unconsciously caused some of the evils which we must remove, can now point the way to the restoration of national prosperity. Education, which — imperfectly assimilated and sometimes ill-directed—has contributed to the ferment of wild ideas from which the world is now suffering, may in time be able to implant an understanding of the fundamental laws of national and industrial economics. It will at least increase the flow from the ranks of manual labour to that of brain work, which is now far more than ever important to industrial and commercial progress" At the conclusion of the address Sir J. J. Thomson in a brief speech referred to the activity of scientific research during the war, and pointed out the necessity for scientific education for all classes, but particularly for those who took a prominent part in the affairs of men. He also drew attention to the changes that were being made in the examination system, from which good results could be expected.

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